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THE
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AND

JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, O.M., D.Sc., F.R.S., &c.

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THE CHEMICAL NEWS.

VOLUME CXII.

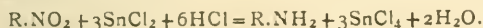
EDITED BY SIR WILLIAM CROOKES, O.M., D.Sc., Pres.R.S., &c.

No. 2901.—JULY 2, 1915.

A MODIFIED REDUCTION METHOD FOR THE VOLUMETRIC DETERMINATION OF NITRO COMPOUNDS.

By A. J. BERRY, M.A., and C. K. COLWELL, B.A.

NITRO compounds are usually determined volumetrically by reduction to amino compounds by excess of a suitable reducing agent, the excess of which is determined by titration in some convenient manner. The reducing agents usually employed for this purpose are stannous chloride or titanous chloride in acid solution. When stannous chloride is employed in presence of hydrochloric acid the reduction proceeds in accordance with the equation—



The excess of stannous chloride is usually determined in an aliquot portion of the solution by titration with iodine after adding excess of sodium bicarbonate and potassium sodium tartrate.

In the course of some experiments on the quantitative reduction of nitro compounds to amino compounds we have applied a method originally due to Weil (CHEMICAL NEWS, 1871, xxiii., 49) for the volumetric determination of copper to determine the excess of stannous halide. This method depends upon the fact that a solution of a cupric salt strongly acidified with hydrochloric acid is reduced quantitatively to the cuprous condition with simultaneous formation of an equivalent amount of stannic salt in accordance with the equation—



It is clear that this method might be applied in the reciprocal way; that is, it should be possible to employ a standard solution of a cupric salt to determine a solution of stannous halide, and, consequently, to determine a nitro compound by difference. The results which we have obtained show that the method is capable of yielding satisfactory results.

In our earlier experiments the general procedure was as follows:—A definite quantity of the solution of the nitro compound was measured out, acidified strongly with hydrochloric acid, and a known excess of a standard solution of stannous chloride added, and the resulting mixture boiled gently for a quarter of an hour, a slow current of carbon dioxide being passed through the solution all the time. The liquid was then titrated at the boiling-point with a standard solution of copper sulphate strongly acidified with hydrochloric acid. The colour of the cupric solution was of course discharged by reduction to the cuprous condition, but it was found necessary to determine

the end-point by testing a few drops of the solution undergoing titration with a saturated solution of mercuric chloride. The end-point was taken as that point at which the solution ceased to give a turbidity with mercuric chloride.

As the employment of an external indicator is a somewhat tedious process we modified the procedure in our later experiments. Etard and Lebeau (CHEMICAL NEWS, 1890, lxi., 137) have pointed out that a solution of a cupric salt acidified with excess of hydrobromic acid possesses a deep brownish violet colour, which becomes perfectly colourless on reduction with a stannous salt. The colour change is much more striking than with hydrochloric acid, and the employment of an external indicator is quite unnecessary. In our experiments we added a measured quantity of a strong solution of potassium bromide to the solution of the nitro compound which was being reduced by stannous chloride and hydrochloric acid. After boiling the solution for fifteen minutes in an atmosphere of carbon dioxide, we titrated the excess of the stannous salt in solution by means of a strongly acid solution of copper sulphate containing potassium bromide. At the end-point of the reaction the liquid assumed an orange-yellow colour, and to obtain strictly consistent results the colour of the solution was compared with that of a dilute solution of potassium dichromate. This second method was found to be much more satisfactory to work than the first, and as far as our experience goes, slightly more accurate also. In both methods the stannous chloride solution was always titrated against the standard copper solution at the time of carrying out a determination.

Examples.

1. *Paranitrophenol*.—1.938 gm. of this substance was weighed out, dissolved in water, and the solution diluted to 250 cc. Aliquot portions of the solution were titrated with the following results:—

25 cc. of the solution with 25 cc. of stannous chloride required 31 cc. of copper solution. 25 cc. of stannous chloride solution alone required 17.6 cc. of copper solution. Hence 13.4 cc. of the copper solution correspond to 25 cc. of the solution of paranitrophenol. The copper solution contained 39.2 grms. of copper (metal) per litre. From this it follows that the weight of paranitrophenol in the 250 cc. of solution is 1.913 gm. This experiment was carried out with the aid of mercuric chloride for determining the end-point.

2. *Picric Acid*.—2.985 grms. of this substance were weighed out, dissolved in water, and the resulting solution diluted to 500 cc. This determination was carried out with the addition of 35 cc. of a 50 per cent solution of potassium bromide to every 25 cc. of the solution of

stannous chloride, and a considerable excess of hydrochloric acid was, as usual, present in every titration. The standard copper solution consisted of 90 grms. of copper sulphate, 50 grms. of potassium bromide, 250 cc. of concentrated hydrochloric acid, and 250 cc. of water, and contained 4.23 grms. of copper (metal) per litre. The following results were obtained:—

25 cc. of the picric acid with 25 cc. of the stannous solution required 31.4 cc. of copper solution. 25 cc. of the stannous solution alone required 14.0 cc. of the copper solution.

From this it is clear that 17.4 cc. of the copper solution correspond to 25 cc. of the solution of picric acid. The weight of picric acid in the 500 cc. of solution is equal to 2.944 grms. It should be pointed out that our experiments demonstrate the applicability of this modified reduction method to the determination of the nitro groups in picric acid. Altmann (*Zeits. Prakt. Chem.* 1901, lxiii., 350) quoted an experiment in which he failed to obtain satisfactory results with picric acid, and concluded that this substance could not be determined by reduction with stannous chloride. The experiments of Knecht and Miss Hibbert (*Ber.*, 1903, xxxvii., 1549) have, however, shown that picric acid as well as other nitro compounds may be accurately determined by means of titanous chloride.

3. *Paranitrophenol*.—1.122 grm. of this substance was weighed out, dissolved in water, and the solution diluted to 250 cc. The acid solution of stannous chloride employed for reduction contained potassium bromide in solution, and the same copper solution as that employed for the determination of the picric acid in No. 2 was employed for the titrations. The following results were obtained:—

25 cc. of the solution of paranitrophenol with 25 cc. of stannous halide required 13.65 cc. of copper solution. 25 cc. of the solution of stannous halide alone required 21.05 cc. of copper solution.

The difference, 7.4 cc. of copper solution, clearly corresponds to the quantity of paranitrophenol in the 25 cc. of solution. From this it follows that the weight of paranitrophenol in the 250 cc. of solution is 1.14 grm.

The few examples which have been quoted are sufficient to demonstrate the possibilities of the method. The experiments were all carried out with measuring vessels which had not been calibrated, and it will be seen that the magnitude of the experimental error was of the order of 1 or 2 per cent. Greater accuracy could doubtless be obtained with more accurate measuring vessels.

Downing College Laboratory,
Cambridge.

THE VOLUMETRIC DETERMINATION OF POLYTHIONIC ACIDS BY POTASSIUM IODATE.

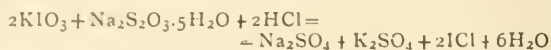
By GEORGE S. JAMIESON.

Sheffield Chemical Laboratory, Yale University.

In a recent paper (*Am. Journ. Sci.*, 1914, xxxviii., 166) from this laboratory it was shown that sulphurous acid could be titrated with a solution of potassium iodate in the presence of 15 to 20 per cent of actual hydrochloric acid and a small volume of an immiscible solvent, such as chloroform, according to the general method of L. W. Andrews (*Journ. Am. Chem. Soc.*, 1903, 25, 756). It has been found that thiosulphuric and tetrathionic acids can be titrated in the same manner, while dithionic acid, on account of its stability, cannot be determined by this method.

In order to test the method for the titration of thiosulphates, a solution containing 3.567 grms. of normal potassium iodate in 1000 cc. was used. (This solution was previously used for the determination of sulphurous

acid mentioned above). According to the equation of the reaction—



1 cc. = 0.002068 grm. of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. The titrations were made in glass-stoppered bottles in exactly the same manner as in the determination of sulphurous acid. It is important to titrate as soon as possible after the thiosulphate is brought in contact with the hydrochloric acid, which should not be warmer than 18° C.; also it is best to dissolve the thiosulphate in a little water previous to adding the hydrochloric acid. For convenience several solutions of sodium thiosulphate of various strengths were prepared and standardised by titration with known amounts of pure iodine in the usual manner, observing all precautions. The results obtained are given in Table I.

TABLE I.

No.	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ taken.	cc. KIO_3 used.	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ found.	Error.
1	0.0506	24.4	0.0505	-0.0001
2	0.0758	36.6	0.0757	-0.0001
3	0.1210	58.5	0.1208	-0.0002
4	0.1011	48.7	0.1007	-0.0004
5	0.0603	29.4	0.0607	+0.0004
6	0.0253	12.3	0.0253	0.0000
7	0.0506	24.5	0.0507	+0.0001
8	0.0253	12.2	0.0252	-0.0001

TABLE II.

1	0.0847	16.0	0.0848	+0.0001
2	0.1008	19.0	0.1007	-0.0001
3	0.0613	11.6	0.0614	+0.0001
4	0.0413	7.8	0.0413	0.0000
5	0.1145	21.6	0.1145	0.0000
6	0.1329	25.1	0.1330	+0.0001
7	0.1554	29.35	0.1555	+0.0001
8	0.1716	32.4	0.1717	+0.0001
9	0.2051	38.7	0.2051	0.0000
10	0.2430	45.95	0.2435	+0.0005
11	0.1923	36.3	0.1924	+0.0001
12	0.1936	36.6	0.1939	+0.0003

The titrations given in Table II. were made with a potassium iodate solution which had the value 1 cc. = 0.005300 grms. of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.

The results in both tables show a satisfactory agreement among themselves and with the actual amounts present.

A volumetric method for the determination of tetrathionic acid has been described by E. Abel (*Zeit. Anorg. Chem.*, lxxiv., 395), which is based upon adding an excess of standard iodine solution to the solution of the tetrathionate, which has been made strongly alkaline. Then the solution is acidified with hydrochloric acid, and the liberated iodine is titrated with a standard solution of sodium thiosulphate in the usual manner. The iodate method has the advantage in requiring only a single standard solution. In order to test the method sodium tetrathionate was prepared according to the method of F. Kessler (*Pogg. Ann.*, 1848, lxxiv., 255), by grinding sodium thiosulphate with a slight excess of iodine in the presence of a few cc. of water. When the sodium thiosulphate was entirely dissolved, two volumes of absolute alcohol were added. After the solution had stood for two hours the sodium tetrathionate crystals were filtered by suction and washed with 98 per cent alcohol until all the iodine and sodium iodide were removed. The sodium tetrathionate was found to contain some sulphate, which was determined by the following method:—Weighed portions of the salt were dissolved in water and acidified with 1 grm. of tartaric acid. Barium chloride was added to the solution, and when the precipitate had settled, it was filtered and determined in the usual manner. The results obtained are given in Table III.

TABLE III.

	Per cent of Na ₂ SO ₄ .
I. 0.3225 grm. sub. gave 0.0181 p.c. BaSO ₄ = 3.31	
II. 0.3330 grm. sub. gave 0.0186 p.c. BaSO ₄ = 3.39	

Average = 3.35

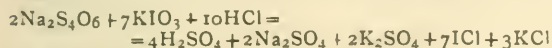
Two water determinations were made at about 112° C.

I. 1.0000 grm. sub. gave 11.27 per cent of water.

II. 0.5000 grm. sub. gave 11.37 per cent of water.

Calc. water for Na₂S₄O₆·2H₂O after correction for 3.35 per cent of Na₂SO₄, 11.35 per cent.

In the analyses given in Table IV., the actual amount of Na₂S₄O₆ present for each titration is stated. The first six titrations were made with the potassium iodate solution mentioned above, which contained 3.567 grms. of KIO₃ in 1000 cc., and according to the equation of the reaction—



the equivalent of the solution is 1 cc. = 0.001287 grm. of Na₂S₄O₆. The sodium tetrathionate was titrated in the same manner as the thiosulphate, except that it was not necessary to take precautions about cooling the hydrochloric acid before adding the tetrathionate. The results obtained are given in Table IV.

TABLE IV.

No.	Wt. of Na ₂ S ₄ O ₆ taken.	cc. KIO ₃ used.	Wt. of Na ₂ S ₄ O ₆ found.	Error.
1	0.0452	35.1	0.0452	0.0000
2	0.0340	26.35	0.0339	-0.0001
3	0.0429	32.2	0.0427	-0.0002
4	0.0612	47.5	0.0611	-0.0001
5	0.0400	30.7	0.0395	-0.0005
6	0.0672	52.0	0.0669	-0.0003
7 (a)	0.0454	13.85	0.0457	+0.0003
8	0.0507	15.3	0.0505	-0.0002
9	0.0640	19.35	0.0638	-0.0002
10	0.0766	23.2	0.0765	-0.0001
11	0.1373	41.7	0.1375	+0.0002
12	0.0872	26.43	0.0871	-0.0001
13	0.1065	32.3	0.1065	0.0000
14	0.0890	26.8	0.0884	-0.0006

(a) Titrations 7 to 14 were made with an iodate solution which had the value 1 cc. = 0.003297 grm. of Na₂S₄O₆.

These results show a satisfactory agreement with the actual amounts of sodium tetrathionate taken.

Dithionates were found to react so slowly with potassium iodate in the presence of strong hydrochloric acid that it was possible to titrate and determine the amount of sodium thiosulphate in the presence of large quantities of potassium dithionate. Likewise tetrathionates could be estimated in the presence of dithionates. The stability of dithionates has been observed previously by R. H. Ashley (*Am. Journ. Sci.*, xxii., 259). It was found that barium and sodium dithionate were only partially decomposed by potassium iodate after reacting for a day and no iodine was liberated for some time after bringing the constituents together. The following experiments were made:—

TABLE V.

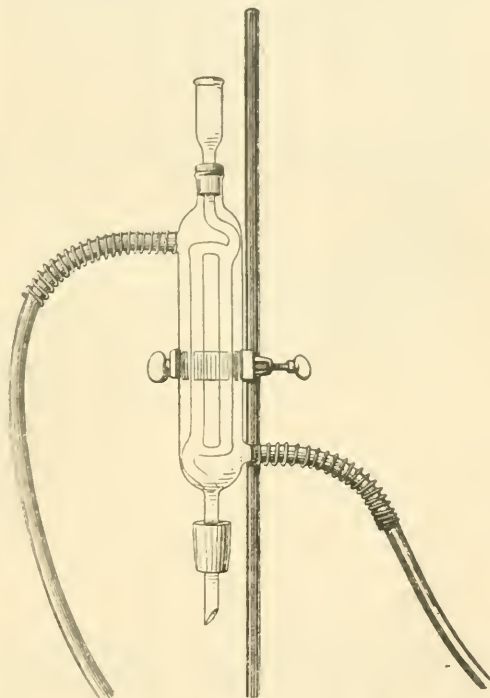
No.	Na ₂ S ₂ O ₃ ·5H ₂ O taken.	K ₂ S ₂ O ₈ taken.	Na ₂ S ₂ O ₃ ·5H ₂ O found.	Error.
1	0.0616	—	0.0615	-0.0001
2	0.0616	0.50	0.0615	-0.0001
3	0.1233	1.00	0.1230	-0.0003
4	0.1849	1.00	0.1851	+0.0002

These results show that the dithionate does not interfere with the titration of the thiosulphate.—*American Journal of Science*, xxxix., No. 234.

A DEVICE FOR OBVIATING THE KINKING OF RUBBER TUBING CONNECTIONS OF WATER JACKETED CONDENSERS.

By A. COTTRELL, M.Sc., and H. WRIGHT, B.Sc.

THE accompanying photograph shows how the rubber tubing attached to condensers can be kept free from the kinks which are so prone to develop at the points of connection.



Brass wire of 15 S.W.G. is wound into a spiral of suitable dimensions, and after being fixed in position the spiral is gently bent to a suitable curve.

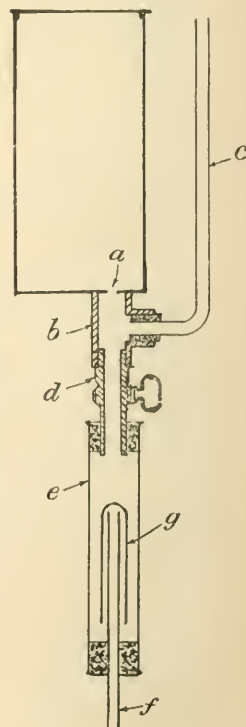
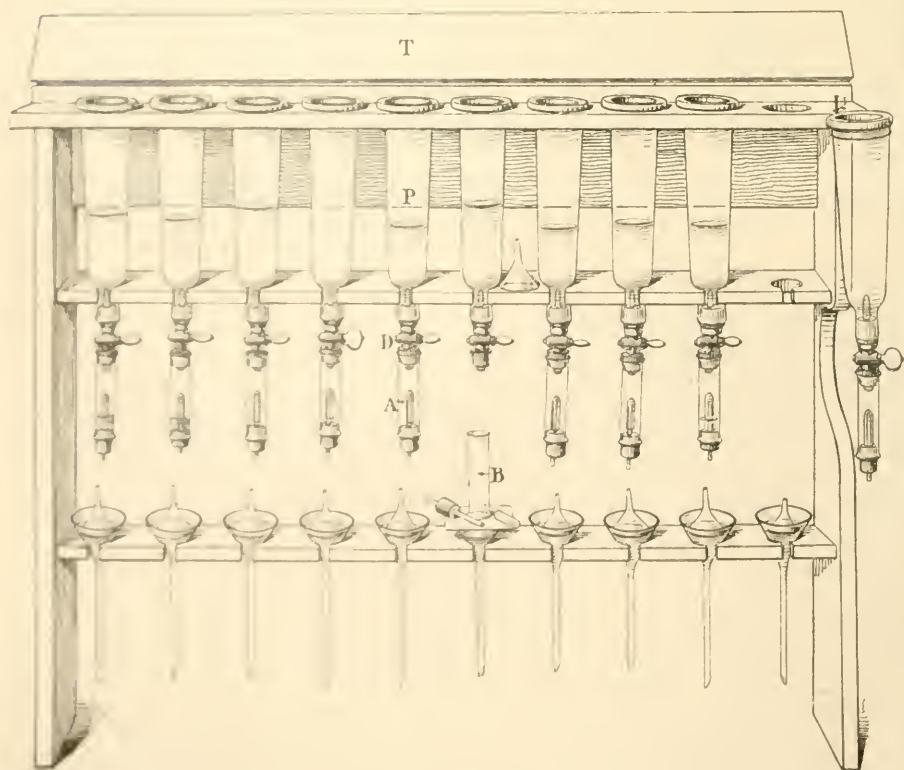
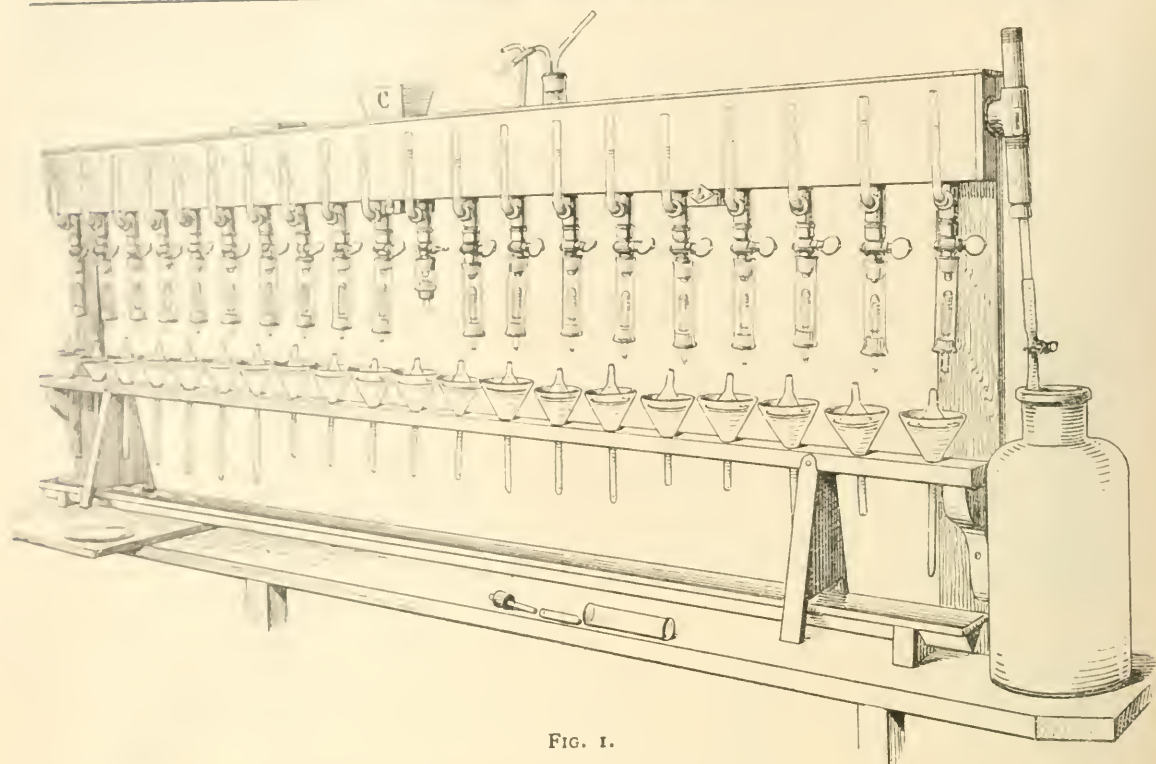
Technical School, Dewsbury.

AN AUTOMATIC FILTER WASHER.

By J. M. PICKEL.

SEVERAL years ago (fourteen) the writer published under the above title a description of an apparatus for washing out of fertilisers, water-soluble ammoniates, and phosphates (*Journ. Am. Chem. Soc.*, xxiii., No. 8; republished in *CHEMICAL NEWS*, 1902, lxxv., 28). Water is dropped from a reservoir intermittently by means of a syphon on a weighed portion of substance on a filter. The nitrogen (or phosphoric acid) in the residue is determined by one of the usual methods; this subtracted from the total nitrogen (or phosphoric acid) gives, of course, the water-soluble portion.

This apparatus, improved and simplified in construction, is still in constant use in this laboratory. Two forms of it are shown in Figs. 1 and 2. In the latter each element (a 300 cc. percolator with its syphon) is separate and distinct, and the charging of each with water requires a separate and distinct operation. In the former, each element is so connected with all the others that all are charged with water by one and the same operation; this effects a material saving of time, where, as in our case, a



goodly number (twenty) elements are operated. The parts of the apparatus are (Fig. 1):—A vessel of sheet copper 160 cm. long, 11.5 cm. deep, and 5 cm. wide (inside). This vessel is provided with a removable lid (which, however, needs rarely to be removed); the object of the lid is to keep out dust. The lid is provided with a hopper-like opening, *c*, which itself has a cap or cover. The vessel is divided into twenty water-tight compartments by partitions, each of exactly the same height (6.5 cm.); each compartment accordingly holds about 260 cc. of water. In the centre of the bottom of each compartment (Fig. 3, section) is a small hole, *a*, about 5 mm. in diameter; over this hole is soldered a galvanised iron tee, *b*. In one branch of the tee is inserted, by means of a cork, a glass tube, *c*, which serves as a water-gauge; into the other branch is screwed an ordinary brass gas-cock, *d* (male, small size). To the nozzle is attached, by means of a cork provided with an air vent, the syphon. The syphon is, preferably, what is known as the engineers' syphon. It consists of a glass tube, *e*, 10 cm. long and 1.8 cm. in diameter inside. The lower end of this tube is fitted with a cork through which passes a small glass tube, *f*, about 4 mm. in diameter inside. This small tube is about 9 cm. long; its upper end is V-shaped (ground sloping on two sides), and extends about 5 cm. into the larger tube. Over the V-shaped tube, and supported by it, is a cap or glass tube, *g*, closed at its upper end, about 7 mm. in diameter inside, and of such length (about 4.5 cm.) that the syphon delivers 10 to 15 cm. of water at each overflow. The flow of water, drop by drop, into the syphon is so regulated by the cock that it (the syphon) delivers water to the funnel underneath more slowly than the water runs out of the funnel. Intermittent washing of the contents of the funnel is thus effected. The inverted small funnel in the larger funnel throws the water around over the edge of the filter-paper. The wash-water is caught by a trough which conveys it into a sink.

The machine is charged by pouring water (distilled) through the opening, *c*; the excess of water, after all the compartments are full, runs out through the overflow, *i*, which is on a level with the tops of the compartments.

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Raleigh, N.C.

THE MOLECULAR WEIGHT OF SODIUM CARBONATE AND THE ATOMIC WEIGHT OF CARBON REFERRED TO SILVER AND BROMINE.*

By THEODORE W. RICHARDS and CHARLES R. HOOVER.

INVESTIGATIONS concerning radio-activity have increased rather than diminished the interest in atomic weights. The possibility indicated by recent research that variations in these figures may exist in radio-active elements stimulates further research in all directions concerning these quantities, for such variations cannot be due to chance, but must have fundamental cause (Richards and Lambert, *Journ. Am. Chem. Soc.*, 1914, xxxvi., 1329; also *Zeit. Anorg. Chem.*, 1914, lxxxviii., 429, and *Science*, June 5, 1914, 831. This conclusion has been supported also by Soddy, *Proc. Chem. Soc.*, 1914, xxx., 134; by Maurice Curie, *Comptes Rendus*, 1914, clviii., 1676; and by Hönigschmid and Mdlle. S. Horowitz, *Ibid.*, p. 1786; also *Zeit. Electrochem.*, 1914, xx., 319). To be sure, no valid evidence of variation in any value, except that for lead, has as yet been found, but whether or not the atomic weights vary in a few cases, they still probably remain the most fundamental figures which come within our scientific ken; therefore no amount of trouble is too great to secure complete and satisfactory knowledge of them.

It is well recognised by everyone conversant with this matter that as many different methods as possible for determining each atomic weight should be employed. F. W. Clarke has often emphasised this point. The difficulty in carrying out this recommendation is that so few substances lend themselves to accurate analysis. Crystalline precipitates always carry down some of the mother liquor from which they were prepared, and hence many usual analytical methods are not permissible when great accuracy is required. For this reason, and so as to get consistent and comparable results with different metals, the analysis of the chlorides and bromides has been one of the chief methods employed at Harvard, because the spongy nature of the silver halides makes it possible to wash them with unusual thoroughness. But some means of verifying these results by comparison with an entirely different standard would be highly welcome. For this purpose a new process, involving cross-reference, has recently been carried out in the Wolcott Gibbs Memorial Laboratory, and the present paper describes this new method of attack.

The plan was simply this:—The purest sodium carbonate was to be weighed with scrupulous care, dissolved in water, and exactly neutralised with hydrobromic acid. The amount of silver necessary to precipitate this hydrobromic acid was then to be determined by the usual process. In this way the chemical equivalence between the weights of sodium carbonate and silver could be simply determined, and the silver halide standard referred directly to an entirely new substance, namely, sodium carbonate. The accuracy of the process turned of course upon obvious criteria: first, the purity of the sodium carbonate and hydrobromic acid; secondly, the complete and exact neutralisation without loss of material; and thirdly, the purity of the silver. The sodium carbonate, silver, and silver bromide alone were weighed, but the hydrobromic acid obviously had to be prepared in a state free from every trace of other acids, as well as from bases. As will be seen, the outcome was very satisfactory.

Preparation of Materials.

In an investigation of this kind the details of experimentation are of the utmost importance, therefore the necessary minutiae are given below.

Three different specimens of sodium carbonate were prepared; the first simply by many recrystallisations from water in platinum vessels, the second from recrystallised hydroxide made by the reaction of sodium bromide on silver oxide, and the third from sodium amalgam electrolytically produced from hydroxide, resulting from the reaction of barium hydroxide on sodium sulphate. In making the first sample, 3 kilogrms. of "C.P." sodium carbonate were dissolved in pure water, filtered while cold through hardened filter-paper, and at first recrystallised four times from pure water in porcelain dishes with centrifugal washing and draining. The solution of the crystals was again filtered as before through washed filter-paper, and recrystallised five times in platinum vessels, again with centrifugal draining and washing. The solution of this ninth crop of crystals was finally filtered through the platinum mat of a carefully prepared Gooch-Munroe crucible and recrystallised, making ten crystallisations in all. The last crop of crystals, contained in a platinum dish, was dehydrated in a vacuum desiccator over fused sodium hydroxide, and was called Sample A.

As briefly suggested above, the second sample, B, was prepared in a very different way. Sodium hydroxide (previously twice recrystallised) was added in excess to twice recrystallised silver nitrate. The washed precipitate of oxide was treated with a solution of sodium bromide, which had been five times recrystallised as hydrate. The resulting sodium hydroxide solution was then once recrystallised from concentrated solution by strong cooling, and was transformed into sodium carbonate by passing pure carbon dioxide into the solution through an inverted platinum funnel. The solution was filtered through a

* Contribution from the Wolcott Gibbs Memorial Laboratory of Harvard College. From the *Journal of the American Chemical Society*, xxxvii., No. 1.

platinum mat and the salt was thrice crystallised. All these operations were carried out in platinum except the crystallisation of sodium hydroxide, which was carried out in silver.

For the sake of especial care, the preparation of the third sample, C, involved yet different processes. Sodium sulphate was added in slight excess to barium hydroxide, each having been previously four times recrystallised. The solution was decanted from the precipitate through a platinum filter and the resulting sodium hydroxide crystallised by cooling. A solution of this sodium hydroxide was electrolysed in an amalgamated iron dish. The solid amalgam after thorough washing was partly decomposed by water, and the solution was evaporated to crystallisation. The pure caustic alkali was transformed into carbonate, as in the case of Sample 2, and the salt thus obtained was thrice recrystallised. All operations except the electrolysis in the iron dish were carried out in platinum or silver.

The hydrobromic acid was prepared from an especially pure sample of potassium bromate, which we owed to the kindness of Edward Mallinckrodt, jun., of St. Louis. Three kilograms of this material, which showed only a trace of chlorine and no iodine, were three times recrystallised in porcelain; even the first crystals gave no test for chloride. Portions of the very pure product were decomposed to bromide by heating in platinum, and the bromide was fused. Proper quantities of bromate, bromide, and very pure redistilled diluted sulphuric acid were gently heated in a glass-stoppered distilling flask. The pure bromine which distilled off was twice redistilled from the similar potassium bromide and passed with hydrogen over hot platinised asbestos. The hydrobromic acid thus formed was dissolved in pure water, concentrated, and three times redistilled through a quartz condenser.

Three samples of silver were used. The first was made from pure silver nitrate by a well tested method (Richards and Wells, Carnegie Inst. of Washington, 1905, Publication No. 28, 19; *Journ. Am. Chem. Soc.*, 1905, xxvii., 475; *Zeit. Anorg. Chem.*, 1905, xlvii., 74). The salt, five times recrystallised, was reduced with ammonium formate prepared from redistilled ammonia and formic acid. The metal was thoroughly washed, dried, and fused in hydrogen on a boat of pure lime made from six times recrystallised calcium nitrate. The buttons were then etched with nitric acid, washed with ammonia and much water, and dried at 400° in a vacuum.

The second sample was prepared with twice as much care, but appeared to be no purer. Silver nitrate, ten times recrystallised, was reduced in a silver dish with ammonium formate, made by passing ammonia from redistilled ammonium hydroxide, contained in a platinum retort, into formic acid, twice redistilled in quartz, contained in a gold flask. The silver powder was washed many times with purest water, then fused and dried, as in Sample 1.

A third sample of silver, prepared by Dr. H. H. Willard in our research on lithium perchlorate, was used in analyses Nos. 4 and 5 (Richards and Willard, 1910, Carnegie Inst. of Washington, Publication No. 125, 16, Sample A).

The quantitative identity of these three samples is evidence that all were as pure as possible.

In a research of this kind, involving exact neutralisation, especial pains must be taken not only with the solid substances concerned but also especially with the water and gases which are employed. Water was thrice distilled, alkaline permanganate and a few drops of sulphuric acid being used in successive distillations as usual. A thoroughly washed condenser of black tin was employed. Especial care was taken to exclude the products of combustion of the burners from the product. For much of the work, where carbon dioxide must be rigorously excluded, the water from the final distillation was condensed in such a way that it was collected cold in a stream of air wholly freed from carbon dioxide. The air used for this purpose,

and in other cases where carbon dioxide must be excluded, was drawn direct from the vent supplying the filtered air to the laboratory before its entry into the room, and was washed and driven by a water blast through a long tube of copper oxide and through Emmerling towers, containing in succession solution of copper sulphate, potassium permanganate dissolved in dilute very pure phosphoric acid, pure permanganate made alkaline by potassium hydroxide which had been fused to drive out volatile substance, and concentrated potassium hydroxide, then over solid fused potassium hydroxide, and finally, where it was necessary to have especial purity and absence of moisture, over fused potassium hydroxide and resublimed phosphorus pentoxide, and over hot copper oxide, being filtered at last through a porous cup to retain dust particles (Richards and Cox, *Journ. Am. Chem. Soc.*, 1914, xxxvi., 819). The apparatus was of course constructed entirely of glass with fused or ground joints.

Carbon dioxide was generated in an Ostwald apparatus by the action of diluted redistilled hydrochloric acid on selected pieces of pure marble. The gas was first passed through three towers containing sodium bicarbonate solution, and afterwards through three towers of boiled concentrated sulphuric acid, to which a trace of potassium dichromate had been added, and finally through a long U-tube of resublimed phosphorus pentoxide.

In one preliminary experiment nitrogen was used. This was prepared by the Wanklyn method of passing ammonia and air over heated copper. The apparatus for this purpose was kindly loaned us by Prof. Baxter and Dr. C. J. Moore. Glass stopcocks were lubricated with a very small amount of a mixture of viscous paraffins, containing a little pure melted rubber, as suggested by Ramsay. They were so arranged that either pure air or carbon dioxide could be passed, separately or mixed, through the familiar Harvard bottling apparatus (Richards, Faraday Lect., *Journ. Am. Chem. Soc.*, 1911, xcix., 1203; see Richards and Parker, *Proc. Acad. Arts and Sci.*, 1897, xiii., 86), and also when needed through vessels in which the solution of the sodium carbonate and the evaporation of the bromide were carried out.

Preparation of Sodium Carbonate for Analysis.

The almost anhydrous carbonate, after long drying in a desiccator over fused caustic alkali, was placed in a weighed platinum boat, covered with a piece of platinum foil, and heated gently in a quartz tube attached to the bottling apparatus. A removable mica sleeve wound with a thin ribbon of a commercial high-melting alloy furnished the necessary heat, with the help of a moderate electric current. After completing the dehydration the platinum foil was removed and the boat and contents were heated for several hours at a gradually increasing temperature until the salt just fused, pure carbon dioxide being passed through the tube. As soon as fusion had taken place the application of heat ceased and pure air was admitted, gradually decreasing the amount of carbon dioxide until when the boat was cold pure air was passing over it. The weight obtained this way was constant after successive trials, which was not the case when the salt was fused in nitrogen or air, a slight gain in weight being usually noted in the latter case. In the presence of air at about 850° fused sodium carbonate attacks platinum to a slight extent, especially if the salt is kept fused for a considerable time. Hoping to avoid this difficulty we used a gold boat in preliminary work, but this steadily gained in weight even after sixty hours' treatment with nitric acid and prolonged ignition in air. Returning to the platinum boat we found that in a stream of pure carbon dioxide free from air it was possible, by very gradually increasing the temperature until the salt was just fused, to prevent any significant action on the platinum boat. Thirteen fusions decreased the weight of the boat only 0.27 mgrm. or 0.02 mgrm. during each fusion.

There is reason to believe that sodium carbonate thus fused in a stream of pure carbon dioxide is purer than

sodium carbonate prepared in any other way. The cooled mass could have contained no excess of carbon dioxide, since the vapour pressure of this gas from the bicarbonate at the temperature employed is enormous; moreover, because the salt came to constant weight on successive fusions there is no suspicion of abnormal loss of carbon dioxide. Because we have been able to find no record of anyone's having prepared the salt in this way before, these samples were perhaps the purest specimens of it which have ever been made. Our experience shows that sodium carbonate as ordinarily prepared for quantitative work is not perfectly dry. Material heated at dull redness for a short time, as usual in most laboratories, was found to lose on fusion sometimes as much as 0.05 per cent of moisture, and even after two hours of such heating the loss was about 0.03 per cent; material heated for a long time just below the fusion-point lost on fusion only about 0.003 per cent. The losses during our experiments ranged between these limits. It is true that for ordinary work such errors are immaterial, but in the most accurate work they become highly important.

(To be continued).

THE MANUFACTURE OF ACID PHOSPHATE.

By WM. H. WAGGAMAN, Scientist in Fertiliser Investigations

(Continued from p. 309).

METHOD OF MANUFACTURE (continued).

The Den System.

THIS system was devised in order that the reactions between the phosphate rock and sulphuric acid might take place rapidly, and yield a dry pulverulent product of high availability (so-called) in the least possible time.

As fast as the charges of acid and rock are mixed they are dropped into a closed brick-lined chamber (den), which is filled to within a short distance of its top. Here the chemical reactions taking place raise the temperature to 120° to 250° C. Carbon dioxide, steam, and gaseous compounds of fluorine work their way out of the mass and escape through the flue at the top of the chamber, leaving the acid phosphate in a dry porous condition.

After standing in the den for about twenty-four hours the reactions are practically complete, and the material is ready to be removed. The heavy wooden doors at opposite sides of the den are then opened, and the acid phosphate is removed. Frequently the floors of the den are so constructed that they can be opened and the acid phosphate discharged into a hopper or upon an acid-proof belt beneath, whence it is taken up by elevators and dumped on the storage pile. The emptying of the den is not only a disagreeable operation, but is attended with considerable danger. The temperature of the acid phosphate contained therein, even after standing from twenty-four to thirty-six hours, is still very high (from 130° to 150° C.), and the fumes given off by this hot material are quite poisonous. Great care must be exercised in digging out the phosphate to prevent large masses of the loose material from falling upon the labourers.

In order to do away with these dangers efforts have been made to empty the dens mechanically. A number of processes have been devised in most of which the excavator or cutter is introduced into the chamber after the acid phosphate is cured (U.S. Patents 892,593, 899,042, 940,583, 949,055, 956,792, 1,013,334, 1,037,404, 1,033,854, 1,070,296). Special forms of chambers are required in some of the processes, while in others the excavating device is adaptable to almost any form of den after the latter has undergone some slight alterations. The more general scheme of emptying the dens mechanically is as follows:—

A device consisting of an endless chain, which either rotates on a shaft or can be moved laterally in the den, is fitted with knives or teeth which cut or break up the acid phosphate and at the same time convey it to a chute. This device is either introduced horizontally at the top of the den or vertically at the side. In the former case the cutter is so arranged that it is mechanically lowered or sinks automatically after completing the circuit of the chamber. If the cutter is introduced vertically at one end of the chamber it cuts away the pile of acid phosphate from the side. It is claimed that the latter method is less likely to cause the material to pack. The removal of acid phosphate mechanically seems to be ordinarily a rather slow process, since the cutters or scrapers, if run at any great speed, cause the material to become heated and gummy. One process of emptying the dens more rapidly consists of a combined cutter and fan. The latter helps keep the material cool while excavation is going on. Another method of emptying the den consists of having the floors mounted on rollers so that one side of the chamber may be swung open and the whole mass of acid phosphate wheeled out and broken up where there is a good circulation of air. Mechanical excavators have not been successfully worked in the factories of this country, however, and the old-style chamber or den is employed almost entirely.

The den system is the only one which can be successfully employed where it is necessary to absorb the fumes given off in the manufacture of acid phosphate. Each den is equipped with a flue near the top, which allows the gases and vapours from the freshly made acid phosphate to escape or be drawn off by means of a fan. The flue leads into a washer or scrubber, which consists either of a wooden tower in which jets of water are constantly spraying, or of a number of compartments through which the gases are made to circulate while they are continually sprayed with water. Under such conditions the gaseous compound silicon tetrafluoride is decomposed with precipitation of silica and formation of hydrofluosilicic acid, as shown in the equation on p. 299. The hydrofluosilicic acid, together with any hydrofluoric acid which may have escaped from the mass of acid phosphate, is absorbed by the water. The acid solution thus produced is used to some extent in the manufacture of fluosilicates of the alkalis which are used in the production of enamel.

Both the initial cost and running expenses of the "den" system are greater than those of the "open-dump" method, but a high-grade product in excellent mechanical condition can be obtained in a short time by the former method without allowing the objectionable fumes to escape into the atmosphere. Most factories are equipped with at least two dens (sometimes four) built close together, with the acidulator or mixer placed on the dividing wall above them. In this way work can be carried on with little interruption, for while one den is being emptied the other may be filled. The capacity of the dens varies from 50 to 300 tons, depending on the size of the mixing plant.

The Open-dump System.

The "open-dump" method is largely used in the South Atlantic States. The mixture of acid and rock is discharged into an automatic dump car and carried to the storage shed, where it is dumped on an open pile. In order that the chemical reactions may get a fair start before the mixture spreads out in thin layers, it is allowed to heat up and thicken somewhat in the mixing pan; frequently it is permitted to remain in the dump car until it has nearly set. Many operators, however, claim to obtain good results by dumping the material almost immediately. Sometimes, in order to prevent the acid phosphate from spreading, a partly open bin is employed. The material after standing in this bin for eight or ten days is taken up by elevators and dumped on a storage pile.

The acid phosphate made by the "open-dump" method

naturally takes much longer to arrive at its maximum availability and optimum mechanical condition. It is usually kept for at least one month before shipping, but adverse weather conditions may delay shipment considerably longer, and even seriously affect the quality of the final product. The production of acid phosphate by the "open-dump" method is impracticable in the vicinity of towns or in a rich farming country unless phosphate rock very low in fluorine compounds is used, for the fumes given off during the process are not only so obnoxious as to constitute a nuisance, but are quite injurious to both animal and vegetable life. At points where these fumes do no harm, however, and where the climate is not too cold, an excellent product is obtained by this method at less cost and with less danger than by the "den" system.

The Drying of Acid Phosphate.

Acid phosphate which is carefully made, especially that produced by the "den" system, seldom requires any subsequent drying. It is customary abroad, however, to dry superphosphates artificially, particularly when they contain an excess of phosphoric acid or are in a poor mechanical condition due to improper mixing. There are two general methods employed in drying acid phosphate. The first consists of the application of artificial heat, and the second of adding some material to take up or combine with the water or free phosphoric acid present.

In Europe a number of machines for artificially drying acid phosphate have been patented. Among the most efficient of these are the dryers of Lutjens, and of Moller and Pfeiffer (Fritsch, "Manufacture of Chemical Manures," 1911, p. 123). In both of these machines the disintegrated acid phosphate is submitted to the action of a current of hot air under pressure. No direct heat can be used in drying acid phosphate because of the tendency of the material to revert at high temperatures.

The second method of drying acid phosphate is often practised in this country when the material is too sticky or wet (due to faulty manipulation) to be uniformly spread on the field or mixed with other fertiliser ingredients. Such a condition when due to an excess of phosphoric acid can be frequently remedied by mixing the sticky mass with small percentages of phosphate rock or limestone. If the condition is due to the presence of a large proportion of iron and aluminium, the addition of finely ground peat or calcined gypsum will dry the material. In expelling the water from acid phosphate by artificial heating the value of the fuel consumed must be added to the cost of production, but no matter how the drying is done it entails additional handling, which is always expensive and should be avoided.

Storing the Acid Phosphate.

In order that the acid phosphate produced may contain a maximum quantity of soluble phosphoric acid when ready for shipment, it is usually stored in well-ventilated buildings for at least two weeks. During this time the quantity of the so-called available phosphoric acid should steadily increase. This is especially true of properly mixed acid phosphate made by the "open-dump" method where the heat is not sufficiently great to bring about rapid chemical reactions.

On the other hand, the storing of acid phosphate for protracted periods in large piles often seriously impairs its mechanical condition and sometimes its chemical composition. The pressure exerted on the material in the lower part of the heap, coupled with its contraction as the mass cools, tends to pack it. When the formation of gypsum is still in progress the superphosphate often becomes so closely cemented that it is difficult to break up. Again, improperly mixed acid phosphate or that high in compounds of iron and aluminium when closely packed is very apt to become gummy or to revert. Porter states that in making acid phosphate by the "open-dump" method the material should not be discharged on the pile until it is stiff enough to "set up" (*Journ. Ind. Eng. Chem.*, 1911, lii., 108).

The storing of acid phosphate in medium-sized piles, however, should cause no trouble, provided it is not allowed to stand too long and the climatic conditions are not unfavourable. Even when the material improves by storing it is hardly economical to keep it over a few months, as the interest on the money invested more than counterbalances the added value of the product due to the increase in available phosphoric acid.

In Table V. the figures of which are taken from Fritsch ("Manufacture of Chemical Manures," 1911, p. 137), the changes taking place in stored acid phosphate made from three different samples of Tennessee phosphate (A, B, and C) are shown.

TABLE V.—Changes taking place in Acid Phosphates made from Tennessee Rock on Storing from Two and a-half to Four and a-half Months.

Sample.	P ₂ O ₅ . Insoluble. Per cent.	Fe ₂ O ₃ + Al ₂ O ₃ .	
		Insoluble. Per cent.	Soluble Per cent.
<i>Composition Directly after Mixing.</i>			
A.	2.27	—	1.16
B.	2.20	1.05	1.34
C.	1.98	1.01	1.57
<i>Composition after Storing for Two and a-half Months.</i>			
A.	2.35	1.21	0.82
B.	2.33	1.20	1.05
C.	2.32	1.17	1.31
<i>Composition after Storing for Four and a-half Months.</i>			
A.	2.30	1.00	1.31
B.	2.23	1.12	1.30
C.	2.48	1.12	1.38

It is not stated whether the acid phosphate was made by the "open-dump" or "den" method, but an inspection of the table will show that little change has taken place in the material after keeping several months. In Table VI. are given the analyses of two piles of acid phosphate sampled after standing certain definite periods of time. The acid phosphate in both cases was made by the "open-dump" system.

TABLE VI.—Analyses of Acid Phosphate from Two Piles after Standing for certain Periods.

Time of storage.	Available phosphoric acid. Per cent.	Insoluble phosphoric acid. Per cent.	Moisture. Per cent.
No. 1.—			
Three days. . .	15.70	2.05	12.80
Ten days. . . .	16.63	1.02	12.70
Six months. . .	16.93	0.47	13.80
No. 2.—			
Thirteen hours. .	15.55	1.50	—
Three days. . .	15.70	1.80	12.60
Six months. . .	17.19	0.18	13.94

Although the percentage of available phosphoric acid continued to increase after storing the material for several months, this increased availability was largely offset by a corresponding rise in the moisture content of the product.

Disintegrating the Acid Phosphate.

Before acid phosphate can be bagged and shipped it must be broken up and put through coarse sieves. In the case of superphosphate which has been carefully made it often suffices to throw the material by means of shovels upon inclined screens, the force of the impact being great enough to disintegrate the lumps. When dealing with acid phosphate, however, which has been improperly made or stored for a long time, it is often necessary to use a machine for breaking up the material. The ordinary crushing devices do not answer for this purpose, owing to the tendency of the acid phosphate to pack or become sticky when pressure is applied, so disintegrators of a special type must be employed.

In a machine (of which an illustration is given in the original) complete pulverisation is brought about by submitting the material to innumerable shocks, but in such manner that no opportunity is given the acid phosphate to pack or gum together.

The disintegrator consists of a number of concentric cages made up of steel bars, all of which are enclosed in a casing. The cages are usually four in number, the first and third attached to a shaft which revolves in one direction, and the second and fourth attached to another shaft having the same axis but revolving in the opposite direction. The casing can be readily opened and the cages slid apart and cleaned.

The acid phosphate is fed through a hopper into the inner or smallest revolving cage, and is thrown by centrifugal force against the bars and into the second cage, which is revolving in the opposite direction. From the second it is thrown into the third, and then into the fourth, finally being discharged from the machine thoroughly disintegrated by the numerous impacts it has received. Two scrapers fitted to the outside cage prevent the material from adhering to the casing and clogging the machine.

After disintegration the acid phosphate is ready to be bagged or mixed with other ingredients to make a complete fertiliser.

COST OF PRODUCTION.

The cost of producing acid phosphate depends on a number of factors, which vary widely. These are the size, location, and equipment of the plant, and the cost of the sulphuric acid employed in the process.

The use of rock mills which grind the largest quantity of rock with the least expenditure of time and power and the employment of mixers having a capacity of 2 tons instead of 1 ton tend to reduce the cost of acid phosphate per ton. Plants located at seaports, where the cost of manufacturing sulphuric acid is less and the price of Florida rock usually lower, can often produce acid phosphate cheaper than those located at inland points. On the other hand, factories located at inland points which are within easy access of the phosphate fields can obtain their phosphate rock cheaper than those more distant from the source of supply. Again, those plants which have their own acid factories can manufacture sulphuric acid cheaper than it can be bought by companies which do not make their own acid.

The initial cost of producing acid phosphate by the den system is greater than by the open-dump method, but since the material can be shipped much sooner when made by the former method, the greater cost is compensated somewhat by the more active capital.

At inland points, such as Atlanta, Augusta, and Birmingham, the cost of producing acid phosphate (16 per cent citrate soluble), exclusive of office expenses, varies from 6.75 to 8 dols. per ton. At seaports, such as Charleston, Savannah, Baltimore, and Norfolk, the cost ranges from 6.20 to 7.50 dols. per ton. In Table VII. is given the cost of producing acid phosphate at a plant running under good conditions located at a seaport and using Florida phosphates.

The figures given in Table VII. were compiled from data obtained through personal inspection of the principal fertiliser factories of the south and east. The costs do not include overhead charges, which vary greatly according to the size and number of the plants run by a company.

DISPOSAL OF PRODUCT.

Acid phosphate is sold on the basis of its so-called available phosphoric acid content, and is worth f.o.b. the factory from 40 to 56 cents per unit, depending on the location of the plant and grade of the product. (The unit is 1 per cent of a ton, or 20 pounds. One ton of 16 per cent acid phosphate contains 320 pounds P_2O_5).

The availability of phosphoric acid is determined by its solubility in a solution of ammonium citrate. There seems

to be no scientific basis for the assumption that the amount of phosphoric acid thus dissolved is equivalent to the quantity which is readily available to crops. It is, however, a convention accepted by the fertiliser trade as well as by many agronomists and agricultural chemists.

TABLE VII.—Average Cost per Ton (2000 Pounds) of Acid Phosphate Manufactured in a Den System Plant Located at Seaport and running at Full Capacity of 500 Tons per week.

Phosphate rock (1133 pounds), at 5.09 dols. per ton	Dols.	2.576
Sulphuric acid (1080 pounds), at 4.75 dols. per ton		2.565
Direct labour		0.264
Five-eighths superintendent's salary		0.091
Power, oil, and waste		0.232
Insurance on 60,000 dols., at 1.55 per cent		0.935
Taxes on 75,000 dols., at 1.25 per cent		0.036
Depreciation on 60,000 dols., at 10 per cent . . .		0.231
Interest on 75,000 dols., at 6 per cent		0.173
Total cost per ton		6.203

The phosphates of South Carolina (27 per cent P_2O_5) and those of Northern Africa (26 to 30 per cent P_2O_5) yield, as a rule, acid phosphate containing 14 per cent available phosphoric acid.

Florida land pebble phosphate gives an acid phosphate containing 16 per cent of available phosphoric acid, and the highest grade rock from Florida, Tennessee, and certain islands in the Pacific Ocean (containing from 35 to 38 per cent P_2O_5) yield a product containing from 18 to 21 per cent of available phosphoric acid.

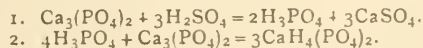
Acid phosphate is usually put up in 200 pound sacks and shipped in closed box cars. The sacks are treated with a solution of silicate of soda, paraffin, or some other substance to prevent the acid phosphate from acting upon them.

The latest official figures on the output of acid phosphate are those for 1909, which show a total production of 3,062,834 tons. It is needless to say that the production has increased enormously since these figures were compiled.

DOUBLE ACID PHOSPHATE.

The double acid phosphate now marketed contains from two to three times as much soluble phosphoric acid as ordinary superphosphate, and is therefore very valuable in the manufacture of concentrated fertilisers. Before the discovery of extensive deposits of high-grade phosphate rock, both in this country and abroad, the making of double superphosphate was widely practised, since it afforded a ready means of utilising low-grade phosphates. Now, however, most of the commercial rock is so high in phosphoric acid that it is unnecessary to resort to schemes for enriching the soluble product obtained therefrom, but in Germany, France, and several other foreign countries, as well as in the State of South Carolina, where a comparatively low grade of phosphate is mined, this process is still used with considerable success.

The two main chemical reactions involved in the manufacture of double acid phosphate are:—First, sufficient dilute sulphuric acid is added to phosphate rock to convert the hypothetical tricalcium phosphate into phosphoric acid and gypsum, and, second, the phosphoric acid thus obtained is used to convert the tricalcium phosphate of a fresh supply of rock into monocalcium phosphate. The reactions in their simplest form may be represented thus:—



The process, however, is by no means as simple as it at first appears, for there are several distinct operations which not only require the watchfulness of a competent superintendent but the control of a skilful chemist.

The phosphate rock and dilute sulphuric acid (16° E.) are run into a vat simultaneously, and stirred thoroughly

for fifteen or twenty minutes. It is inadvisable to use warm acid to decompose the rock or to stir for a protracted period, since under such conditions the compounds of iron and aluminium are dissolved only to be precipitated again later on, causing the reversion of a part of the phosphoric acid. The quantity of sulphuric acid required to bring about the desired reactions should be carefully ascertained from analyses of the raw material, since either an excess or an insufficient quantity will cause trouble in the subsequent operations.

The muddy solution is run into a tank from which it is pumped to a filter-press where the sediment and gypsum is separated, the clear phosphoric acid solution being run into evaporating pans. The residue in the filter-press is then washed with water till the washings have a concentration of 0.25° B. or less. These washings are used to dilute the sulphuric acid employed in the process.

Before the phosphoric acid produced can be used for making double acid phosphate it must be concentrated. This is usually done by evaporating in iron pans lined with stone or some acid resisting material. After concentrating to about 56° or 58° B., it is run into lined-lead tanks from which it is drawn or pumped as required. The mixing of this phosphoric acid with phosphate rock and all subsequent operations are practically the same as those employed in making ordinary acid phosphate, but the final product often has to be artificially dried since it contains but a small percentage of gypsum. Ordinary acid phosphate, as we have seen, is largely a mixture of soluble lime phosphate and gypsum, the latter having been formed from calcium sulphate by extracting the excess of water from the mass. Double acid phosphate, however, consists chiefly of soluble lime phosphate with but little calcium sulphate to act as a dehydrating agent, and therefore requires artificial heating to drive off the excess of water.

(To be continued).

ELECTROLYTIC DISINFECTANT.*

THE following Report is submitted at the request of the Council:—

The initial cost of the apparatus, building, &c., in 1906 was £583 9s. 2d.

Initial outlay (plant)	£325	0	0
Fittings, &c. (Electricity Department)	71	7	11
Sundries, Structural (Electricity Department) ..	6	6	11
Sundries Electricity Department)	4	6	11
Structure of Depot (Works Department) ..	120	6	11
Sundries	32	4	7
Carboys	23	16	9

£583 9s. 2d.

On account of the great demand for the electrolytic fluid the Depot had to be enlarged, and an additional new plant, with electric motor for stirring, and switchboard, &c., was installed at the beginning of 1910, and, with alterations to the first plant, cost in round figures £500. Owing to the extension of the Electricity Works the whole structure and installation had to be dismantled, and was re-erected on the opposite of the Violet Road.

During the working of the apparatus, a period of nine years, many improvements for the municipal success of the installation have been made, the expenses of which come under the heading of "Sundries and Petty Expenses" in the table of the average expenditure for the three years ended March 31, 1914.

Among the improvements a very important one has been introduced for the reception of the fluid from the electrolyzers. Instead of the glass receptacles, which are

apt to break and are very costly, specially made cheap metal drums have been substituted.

A double cell has been constructed of slate, in such a form that the "creeping" of the current (which comes direct from the Council's mains) from one cell to another is prevented. This is a most important item. All slate contains metal, and the current in "creeping" from the electrodes in one cell to the electrodes in the other cell causes erosion to take place, and sooner or later a "dead short" happens and a new double cell is required, which is an expense.

The present cells are earthenware and replaced the original slate ones, and were made by a firm of potters in the Borough at the special request of the Medical Officer of Health and under his direction and supervision, potters outside the Borough having refused to make them, as they stated the baking would be a failure. However, the tanks or cells were made, and, as stated above, are the present ones, having been in use for some years. Electricity, on account of moisture, will even creep with an earthenware cell and efficiency will be lost, and if the partition of the earthenware cell or tank is not properly glazed it will in course of time become destroyed by the electrical current (240 volts and 20 amperes) acting upon the fluid, which soaks into the unglazed earthenware. Earthenware cells take a long time to make (possibly four months), and one is never certain that in the firing of earthenware there will not be defects in the articles when they are taken out of the kilns. A slate double cell can be made in a few days, is cheap, and as now constructed will not permit the current to "creep" and erosion to take place, whereby we have cheapness, safety, and greater efficiency. The current being taken direct from the Council's mains saves the expense of a "converter," with its consumption of current and necessary skilled attention.

Since the installation of the plant 381,794 gallons of fluid have been manufactured, at a cost for electricity of £401 19s. 1d. and materials of £345 9s. 11d. (under ½d. per gallon).

The Public Health Department is not only furnished with the electrolytic disinfectant, and the various institutions of the Council (the public baths, &c., and the Works Department as required), but the institutions of the Managers of the Sick Asylum and of the Board of Guardians (within and without the borough) are supplied with an unlimited quantity free; also some of the London County Council public elementary schools.

Report of a Committee of the Royal Sanitary Institute, re the Purification of the Water of Swimming Baths, November, 1912.

"The Committee also investigated the treatment of bath water by electrolytic fluid, which is in use at the Poplar Baths, and was very much impressed by the good results obtained. By the addition of hypochlorite of magnesia solution to the pond water, in amount sufficient to give one part of free chlorine to every one or two million parts of water, not only is the water sterilised, or deprived of all organised living molecules, but it is kept sweet and free from odour, and there is no tendency in the water to the deposition of slimy sediments on the floor of the pond. A certain amount of slimy matter collects on the walls of the pond at the line where the surface of the water is in continual movement from the undulatory motions induced by the movements of the bathers, but this is readily removed with a swab by an attendant. . . . It should be said that the electrolytic fluid in the Poplar Baths is not used with idea of rendering unnecessary periodic changes of the pond water, but to keep the water in the pond fresh and free from harmful organisms all the time it is in use. The class of persons who use the swimming ponds in Poplar is always likely to contain uncleanly or infected individuals, and it is to guard against danger from the latter that the fluid finds its chief application."

Respecting the stability of the fluid as manufactured in Poplar, a long article appeared in the *Lancet* of January 18,

* Report to the Public Health and Housing Committee, Metropolitan Borough of Poplar, June 1, 1915.

1908, under the heading of "Electrically Produced Fluids containing Hypochlorites: their manufacture, and the rationale and chemistry of the process for securing stability." It is well known that the fluid as made in Poplar is rendered stable for an almost indefinite period, and is suitable either for municipal or for commercial purposes. The rendering of quantities of hypochlorite of magnesia electrolytic fluid stable for municipal purposes was the difficulty which had to be overcome with the plant erected in Poplar, because no plant was in existence prior to the Poplar plant where this had been done on a large scale. Upon the visit to Rolleville, France, in the year 1905, after the first report of the Medical Officer of Health to the Council, the then Chairmen of the Public Health, Electricity, and Works Committees—Messrs. A. G. Smith, J. Bussey, and F. Thorne respectively—and the Electrical Engineer and the Medical Officer of Health, a small plant for making a medical solution was exhibited, but this plant was indeed very different to the one supplied to the Poplar Borough Council, and could not possibly have made fluid in quantities sufficient for municipal purposes. This small plant at the time of visit was stated to have broken down, being not at work.

The success which has attended the working of the plant has been largely due to the loyal support and mechanical ability of the chief disinfecter, W. D. Quested, and also to the interest and care displayed by C. Hagon, who has the immediate charge of the apparatus during the manufacture of the fluid. J. Harber, the labourer, has also paid great attention to the work, and can be entrusted with the management of the machines when necessary.

The work of making electrolytic disinfectant as carried out in Poplar has been appreciated. Plants have been supplied to Guernsey, Gateshead, Finland, Buenos Ayres, and Rangoon. At Port-mouth a plant has been installed for manufacturing the fluid direct from sea-water, and rendering it stable by the method adopted in Poplar. Recently the Finchley Council placed an order for an installation.

Shortly after the commencement of the war the question of obtaining the necessary materials for the manufacturing of the electrolytic disinfectant was considered, as chloride of magnesium had been obtained in the past from Germany. The normal price is £4 5s. per ton delivered free at the depot, but the price went up to £14, the present price ranging from £11 to £14 per ton. Three tons were secured at £4 8s. per ton, one ton at £6, and seven tons at £7 5s. per ton.

With regard to other materials, ten hundredweight of caustic soda was procured at an increase of ½d. per lb., to be delivered in quantities of 192 lbs. as required. Ten tons of salt, the usual price of which is £1 14s. per ton, were obtained at an increased cost of 2s. 6d. per ton for cartage.

It is estimated that the present stock of the above materials—with the exception of caustic soda, which can be obtained as required—will last twelve or fifteen months.

WELSH NOTES.

(By Our Special Correspondent).

It is a significant indication of the way in which trade generally is being maintained at the Swansea Docks that the total tonnage for last week only just fell short of the total for the corresponding period of last year, which was an exceptional one. Imports were quiet, but the coal and patent fuel exports displayed considerable activity. Noticeable among the imports was a 4460 tons cargo of iron pyrites from Spain. Shipments of patent fuel amounted to 15,791 tons, tinplates and general goods 14,325 tons. Boxes of tinplates received from works aggregated 77,433, whilst 226,850 represented the stocks in dock warehouses

and vans. Shipments amounted to 163,439 boxes. Minor imports included 514 tons scrap iron and steel, 335 tons pitch, and 400 nickel metal.

As has been the case during the past few weeks, great activity was everywhere observed in the Swansea Valley during the week, the chief complaint being a lack of labour. At the Landore Blast Furnaces the men were engaged for very long periods in order to cope with the work, and it is safe to say that not for many months has the steel trade of the Swansea Valley experienced such great pressure. The copper trade was satisfactory, all refineries being fully engaged, and a high yield of copper plates followed. A good demand prevailed for all classes of material at the various spelter works. Tinplates brightened up very considerably, the Duffryn, Forest, Beaufort, and Worcester works being fairly well maintained, although occasional stoppages took place at the Upper Forest Works. The bar mills and sheet trade, however, were still unaltered. The safety fuse works and lead-pipe works were very brisk indeed, and all departments of the Mond Nickel Works were fully employed. The Mannesmann Tube Works were having a good call for material. As usual, however, the sulphuric acid factories were very slack, there being very little demand for vitriol. Metal extraction works were kept going fairly well.

Port Talbot Dock trade was satisfactory, although a small decrease in comparison with the corresponding period last year was registered. Patent fuel exports totalled 3,304 tons, whilst chief among the imports were 1300 tons pitch and 1608 tons pig-iron. Tinplates as usual were very dull, but the Morfa Copper Works were running at high pressure, a great deal of Government work being in hand.

At the Dowlais Works all departments were very busy during the week. The Goat Mill was engaged on heavy steel rails, steel sleepers, and billets, and some tin-bar, sole-plates, and steel bars were also run there. The Big Mill turned out a fine crop of short steel bars, rails, and curves, and a quantity of fish-plates. The Blast, Bessemer, and Siemens furnaces were also busy. The finishing departments were well employed, and the dispatching of the finished material was done with smartness.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, June 17, 1915.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"Soil Protozoa and Soil Bacteria." By E. J. RUSSELL.

In view of the claim recently made by Goodey that soil protozoa cannot function as a factor limiting the numbers of bacteria in soils, the author has brought together the evidence on which this view is based.

It has been shown in numerous experiments that the numbers of bacteria in normal soils are relatively low, but they can be raised by any treatment that kills trophic forms and not spores. Starting, in the first instance, to find the properties of the factor which keeps down the bacterial numbers, and without framing any hypothesis as to its nature, these were found to be: (a) active, and not a lack of some essential; (b) not bacterial; (c) extinguished by heat or poisons, and after extinction does not reappear; (d) can be reintroduced by adding a little untreated soil; (e) is favoured by conditions favourable to trophic life in the soil.

These properties indicate that the factor is biological. Search was therefore made for organisms fulfilling these conditions, and numbers of protozoa were found. Definite evidence has been obtained that trophic forms occur as normal inhabitants of the soil, and the estimates of num-

bers so far available show that they are considerable. There is the closest possible relationship between the extinction of the protozoa and the extinction of the limiting factor, and also between the re-establishment of the protozoan fauna and the setting up of the limiting factor after reinfection with small quantities of soil.

Hitherto the reinfection with mass cultures of selected protozoa has not had the effect of reducing bacterial numbers, but this is attributed in part to the difficulty of obtaining a suitable control, and in part to the fact that the fauna developing in culture infusions (from which the organisms were selected) differs from the trophic fauna, the forms predominating in the one not necessarily figuring largely in the other. Until more is known of the life-history of the protozoa of the soil, it is unsafe to attach too great importance to failure of reinfection experiments made with mass cultures of forms prominent in hay-infusion cultures from the soil.

"The Enhanced Series of Lines in Spectra of the Alkaline Earths." By Prof. W. M. HICKS, F.R.S.

A discussion of the enhanced series of the alkaline earths is carried out in order to determine their relation to the oun. For this purpose the results given for Mg, Ca, Sr, by Fowler in his recent Bakerian Lecture are used, and, in addition, the corresponding series in Ba and Ra are considered. It is found that the quantity Δ' , giving the doublet separations, is given with great accuracy in terms of the oun, as follows:—

Mg, $56\frac{1}{2}\delta$; Ca, 68δ ; Sr, 58δ ; Ba, $56\frac{1}{2}\delta$; Ra, $60\frac{1}{2}\delta$, where δ is four times the corresponding oun for the element.

The satellite separations are also found as functions of the same quantity. Further it is shown that these series strongly support the general relations given in a former communication that the first p -sequence depends on a multiple of the atomic volume, and that the diffuse sequence is such that the denominators of the first lines, when the wave number is expressed in the form— $A-N(\text{den})^2$, are themselves multiples of Δ' or of the oun.

"Certain Linear Differential Equations of Astronomical Interest." By Prof. H. F. BAKER, F.R.S.

"On the Partial Correlation-Ratio." Prof. KARL PEARSON, F.R.S.

"Effect of Temperature on the Hissing of Water when Flowing through a Constricted Tube." By S. SKINNER and F. ENTWISTLE.

The experiments deal with the temperature coefficient of the effect described by Osborne Reynolds before the British Association at Oxford, 1894. It is shown that the velocity at which hissing just occurs between 0° and 100° C. suffers a diminution which may be expressed by a formula $V_t = -c(t - \theta)$ where V_t is the velocity of the stream at a temperature t , and θ the critical temperature of water, and c a constant. It is argued that this result forms a measure of the tensile strength of the liquid, and consequently it brings the phenomenon of hissing into relation with the other properties of a liquid.

"Ionisation Potentials of Mercury, Cadmium, and Zinc, and the Single and Many lined Spectra of these Elements." By J. C. McLENNAN, F.R.S., and J. P. HENDERSON.

1. It is shown that a spectrum consisting of a single line is obtainable for mercury, for zinc, and for cadmium.

2. The wave-lengths of these lines are for mercury $\lambda = 2536.72$ A.U., for zinc $\lambda = 3075.99$ A.U., and for cadmium $\lambda = 3260.17$ A.U.

3. The minimum ionisation potentials for mercury, zinc, and cadmium are shown to be 4.9 volts, 3.74 volts, and 3.96 volts respectively.

4. Some considerations are presented which support Sir J. J. Thomson's theory of the two-type ionisation of atoms of mercury, and others which suggest that the theory is applicable as well to the ionisation of atoms of zinc and cadmium.

5. The minimum arcing potential differences which will bring out the many-lined spectra of mercury, zinc, and cadmium vapours are found to be 12.5 volts, 11.8 volts,

and 15.3 volts respectively. These voltages are also probably the minimum ionisation potentials of the second type for the atoms of these three elements.

6. Considerations are presented which suggest the possibility of analysing the spectrum of an element in such a way as to enable one to correlate different portions of the spectrum with disturbances in definite portions of the atomic structure of that element.

"The Monoclinic Sulphates containing Ammonium." Completion of the Double Sulphate Series. By A. E. H. TUTTON, F.R.S.

In this communication are described the five remaining double sulphates of the series $R_2M(SO_4)_2 \cdot 6H_2O$, in which R is ammonium and M is nickel, cobalt, manganese, copper, and cadmium. The present memoir completes the author's work on the double sulphates of this series.

The main conclusions are the following:—

1. These ammonium salts are truly isomorphous with the similarly constituted potassium, rubidium, and caesium salts of the generic formula above given, but are not eutropic with them; the potassium, rubidium, and caesium salts alone form the exclusive eutropic series in which the crystallographical properties (both morphological and physical) obey the law of progression with the atomic weight of the alkali metal which has been established in previous communications. This law is particularly well illustrated by the fact, to which no exceptions have been observed, that average change of angle between crystal faces, and also maximum change of interfacial angle (which exceeds two whole degrees), are directly proportional to change to atomic weight when any one alkali metal is replaced by another.

2. The dimensions of the space-lattice of any ammonium salt of the series are nearly identical with those of the intermediate rubidium salt, so that the two atoms of rubidium are replaced by the ten atoms of the $2NH_4$ radicle groups without appreciably altering the crystallographic structural dimensions.

3. The salts of the series in which R is thallium (also studied in a previous memoir) resemble the ammonium salts closely, in truly belonging to the isomorphous series, but not to the more exclusive eutropic series formed by the salts of potassium, rubidium, and caesium. Like the ammonium salts they also closely resemble the rubidium salts, but the thallium salts are distinguished optically, possessing transcendent refractive power, both their refractive indices and their molecular refraction being far higher than for any other salts of the whole isomorphous series.

"General Equations for the Neutralisation of Dibasic Acids, and their Use to calculate the Acidity of Dilute Carbonate Solutions." By E. B. R. PRIDEAUX.

"Electrical Conductivity and Luminosity of Flames containing Salt Vapours." By Prof. H. A. WILSON, F.R.S.

"Spectrum associated with Carbon in Relation to the Wolf-Rayet Stars." By T. R. MERTON.

"Threshold of Vision for Different Coloured Lights." By Sir WILLIAM ABNEY, F.R.S., and Prof. W. WATSON, F.R.S.

"Hydrodynamical Problems suggested by Pitot's Tubes." By Lord RAYLEIGH, O.M., F.R.S.

1. *Electrical Effects accompanying the Decomposition of Organic Compounds.* 11.—*Ionisation of the Gases produced during Fermentation.* By Prof. M. C. POTTER.

"Inheritance of Colour in the Stick-Insect (*Carausius morosus*)." Prof. E. W. MACBRIDE, F.R.S., and A. JACKSON.

"Relation between Transpiration and Stomatal Aperture." By Sir FRANCIS DARWIN, F.R.S.

"The Monotreme Skull—a Contribution to Mammalian Morphogenesis." By D. M. S. WATSON.

THE CHEMICAL NEWS.

VOL. CXII., No. 2902.

MATTER, MASS, WEIGHT.

By H. STANLEY REDGROVE, B.Sc. (Lond.), F.C.S.

MR. F. H. LORING's paper, "Mass and Weight," published in the CHEMICAL NEWS for June 25 (vol. cxii., 301), raises one or two points of considerable interest.

Mr. Loring, following the older school of physicists, defines "mass" as "a term for the quantity of matter in a body." This definition is open to more than one serious objection. In the first place it lacks precision, owing to the ambiguity of the word "matter." Indeed, the word "matter," as Ostwald has pointed out, is so closely associated with metaphysical ideas as to be quite unsuitable for usage in the physical sciences. Secondly, the objection may be raised that the application of the concept "quantity" to matter needs justification; and lastly, it may be urged that, allowing this application, the usual manner of measuring "mass" (*i.e.*, as proportional to the force producing a standard acceleration in the body), by no means follows from the definition, and rests on the merest assumption. If we examine the various definitions of matter which have been put forward we shall find that many of them are incapable of quantification, and the one which is most readily quantifiable—namely, "matter is extended substance"—gives *volume* as the measure of quantity of matter. Indeed, to give Mr. Loring's definition of "mass" any semblance of justification, "matter" must be defined in a sense wholly divorced from common usage.

The underlying assumption of this definition of mass seems to be that there is some constant and persistent element in experience. This having been termed "matter," "quantity of matter" is assumed to be proportional to the force producing a standard acceleration in the body because of the constancy of that force.* But the *petitio principii* is evident when we are told that the indestructibility or persistence of matter is demonstrated by means of this constancy. Mr. Loring does not, indeed, say this, but it is what is commonly asserted, and what I think he has in mind. As a matter of fact, however, nothing is constant, and there is no persistent element in experience, save the unity of consciousness wherein the diverse elements of experience meet.

If, however, we throw overboard Mr. Loring's definition of "mass" and attend only to his description of how it may be measured, the whole matter becomes much clearer. And the first thing that must strike one is the identity of "mass" and "inertia." We say that a body possesses "inertia" because force is needed to accelerate (either positively or negatively) its motion. Precisely. Therefore "inertia" is measured by the force producing a standard acceleration in the body, or alternatively by the reciprocal of the acceleration produced by a standard force; in short—

$$m \propto \frac{P}{f}$$

where m = inertia, P = force, and f = acceleration.

If "mass" is defined in precisely similar terms, as, for instance, in Poynting and Thomson's "Properties of Matter," being thus identified with "inertia,"† the ordinary method of measuring mass follows at once from the

* Not constant, however, under all conditions (namely, when the velocity approaches that of light; *vide* Kaufmann's experimental verification of Sir J. J. Thomson's calculations.

† It would conduce to clarity of thought if one of the terms, preferably "mass," could be permanently abolished as unnecessary.

definition, the constancy of gravitational acceleration being established for any given point of the earth's surface. Needless assumptions are thus avoided. This matter I have more fully dealt with in Chapter I. ("On the Indestructibility of Matter") of my "Matter, Spirit, and the Cosmos" (Rider, 1910) and "Is Matter Indestructible?" (*Knowledge*, 1912, xxxv., 292).

Before proceeding to my second and last point I want to clear up one or two matters concerning the units of mass (inertia) and weight. The pound, gramme, &c., are units of mass (inertia), defined by certain standards kept in London and Paris, as stated by Mr. Loring. They are *not* units of weight, although commonly spoken of as such. The units of weight are the units of force, *i.e.*, the poundal and the dyne (the force required to accelerate 1 pound 1 foot per second per second, and the force required to accelerate 1 grm. 1 cm. per second per second respectively). Now, if g is the acceleration due to gravity, the weight of a body whose mass (inertia) is 1 lb. is g poundals, similarly the weight of a body whose mass (inertia) is 1 grm. is g dynes. Since g is almost constant (32 ft. per second per second = 981 cm. per second per second), the weight of a body whose mass (inertia) is 1 lb., and the weight of a body whose mass (inertia) is 1 grm., are practically constant, and for this reason are taken as units of weight in everyday matters, thus leading to the confusion as to units already mentioned. But just because g is not quite constant (and in extreme circumstances varies very greatly) such units are unsuitable for use in the science of mechanics; hence the need of the poundal and the dyne.

My second point is that the expression "ratio of mass to weight" is inadmissible, because a ratio is defined as the relation between two quantities of like kind, and mass and weight are not of like kind. We could, indeed, speak of the ratio between the numbers expressing the mass and the weight of a body, but then this ratio would depend entirely upon the units of measurement chosen, and could become unity by a simple change of units. That is all Mr. Loring's example on p. 303 amounts to. He speaks of his "gramme standard of platinum" as having "a weight of 1 grm.," by which is meant, presumably, the weight (in the given circumstances) of a body whose mass (inertia) is 1 grm.; and speaks of the ratio of its mass to its weight as being unity. But just as truly this ratio is about $\frac{1}{32}$ if one uses the dyne as the unit of weight, or about $\frac{1}{981}$ if one uses poundals and pounds, or any other number.

Weight is a purely relative term. A body has no weight in itself, but only in reference to other bodies. What a body weighs (P) is dependent not only upon its mass (inertia = m_1) but also upon the mass (inertia = m_2) of the other body, with respect to which it exhibits that weight, as well as the distance between the centres of gravity of the bodies (d), according to the "law of gravitation"—

$$P \propto \frac{m_1 m_2}{d^2}$$

Nor is mass (inertia) an absolute property of a body. This only exists in relation to the forces acting on the body, and, as Thomson and Kaufmann have proved, is not a true constant. Indeed, as I have tried to show in "The Magic of Experience" (Dent, 1915), we know no isolated facts, but only the relations between them—therein experience consists and therein truth abides.

West Ham Technical Institute.

Royal Institution.—A General Meeting of the members of the Royal Institution was held on the 5th inst., the Duke of Northumberland, President, in the Chair. Mr. William H. Glaser and Mrs. Skinner were elected Members. The Managers reported that they had re-elected Sir James Dewar, M.A., D.Sc., LL.D., F.R.S., Fullerian Professor of Chemistry for a period of three years.

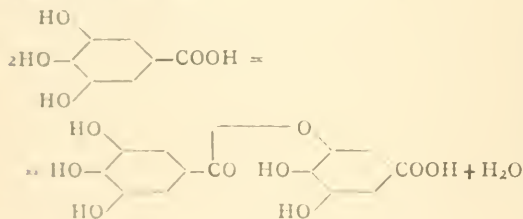
RECENT SYNTHETIC STUDIES IN THE TANNIN GROUP.*

By F. J. MOORE.

THERE exist in nature a considerable number of substances whose aqueous extracts have the property of turning hide into leather. Substances which show this property have also certain other general characteristics. Tanning substances are amorphous and have an astringent taste. They usually precipitate gelatin from its solutions and form compounds with metals, those with iron, for example, being frequently coloured and suitable for use as inks. Hydrolytic agents split them into a variety of products. One of these is almost always a sugar, usually *d*-glucose, while the other component is some hydroxy acid of the aromatic series. Caffeotannic acid, for example, which is found in coffee and Paraguay tea, yields a sugar and caffeic acid. The tanning material of oak bark yields ellagic acid and quecicite. Still others yield phloroglucinol instead of sugar.

The most thoroughly studied of these substances is ordinary tannin, which occurs in the nut-galls of the oak and is also found in sumach, tea, and other plants. It is a colourless, amorphous substance, which is readily soluble in water and only slightly soluble in alcohol and ether. It can be prepared in a state of comparative purity, and its structure has interested organic chemists for a long time.

The most important of the earlier investigations was carried on by Strecker in 1852 (*Ann. der Chemie*, 1852, lxxxi., 248; 1854, xc., 328). He hydrolysed tannin and found three molecules of gallic acid associated with one of *d* glucose. Many chemists who studied the problem later came to the conclusion that sugar was not an essential constituent, at least in all kinds of tannin, and the observation that gallic acid, by means of phosphorus oxychloride and other dehydrating agents, could be changed to digallic acid—



led Schiff, in 1871 (*Ber.*, 1871, iv., 232, 967; 1879, xii., 33; and *Ann.*, 1873, clxx., 43) to accept this synthetic digallic acid as, at least, the principal component of tannin. Such a conclusion left the optical activity of tannin unexplained, since digallic acid contains no asymmetric carbon atom. It could not be certain, however, that optically active impurities might not be present, inasmuch as tannin is an amorphous substance and the usual criteria of purity and homogeneity in organic substances are lacking.

Walden, in 1897 (*Ber.*, 1897, xxx., 3151; 1898, xxxi., 3167), made an extensive comparison of the synthetic digallic acid with tannin, and found that their physical properties were not identical. The molecular weight of tannin is far too great for digallic acid, and neither the electrical conductivity, the absorption of light, nor the behaviour with arsenic acid were found sufficiently parallel for Walden to believe in the identity of the substances concerned. Quite recently, Nierenstein made the suggestion that tannin might be a mixture of digallic acid with its optically active reduction product, leuco-tannin. Such a mixture, however, should be more acidic than

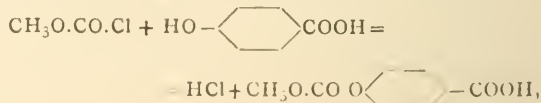
tannin and have a smaller apparent molecular weight. Still more recently Feist (*Ber.*, 1912, xlv., 1493) has suggested a more complex composition, but his conclusions have now been superseded by the work of Emil Fischer (*Gen. résumé, Ber.*, 1913, xlv., 3253; see also 1908, xli., 2875; 1912, xlv., 915, 2709, 3773; 1913, xlv., 1116), which it is the principal object of this paper to describe.

Emil Fischer's attention was first devoted to the purification of tannin with the idea of obtaining as homogeneous a material as possible. For this purpose, the purest product from Chinese nut-galls was shaken from a dilute alkaline solution by ethyl acetate. It is obvious that a substance so purified could contain no free carboxyl group, and we can assume this to be the fact concerning the material investigated by Fischer. When purified in this way, the substance is amorphous, but it is doubtless as pure a tannin as has hitherto been prepared. It is optically active, the specific rotatory power being about 70°.

The next step was the hydrolysis of tannin. This was carried out in acid solution, since alkali would act upon any sugar formed. The method was checked by blank tests made with mixtures of gallic acid and sugar, and after making any necessary corrections of this kind, it was found that hydrolysis had decomposed the tannin into a mixture of one molecule of *d*-glucose and ten of gallic acid. No other hydroxy acid was found. Since there are five hydroxyl groups in *d*-glucose, a simple interpretation of the results would suggest that we had to do with an ester of glucose in which each of the five hydroxyl groups was esterified with a molecule of digallic acid. Such a substance would not be a glucoside in the ordinary acceptance of the term. Emil Fischer is of the opinion that the latter name should be reserved for products analogous in their structure to methyl glucoside—

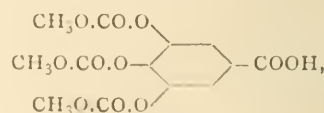


The best proof of the structure suggested for tannin would be its synthesis, but in view of the difficulty of preparing synthetic digallic acid, it seemed best to begin with the simpler problem of preparing glucose pentagallate. The method which first suggests itself for the preparation of such a compound is the treatment of the sugar by the chloride of the acid; but chlorides of substances like gallic acid are difficult to prepare. The usual easy reaction of the chlorides of phosphorus upon the free acids is complicated in this case by the fact that the hydroxyl groups also present are attacked by the reagent. Emil Fischer was able to avoid this difficulty by a method which he had previously used in less complicated cases. This consisted of treating a hydroxy acid with methyl chlor-carbonate. This forms a carbomethoxy derivative—



which is stable enough to tolerate reactions upon the carboxyl group, but when these reactions have been carried out, gentle hydrolytic agents exchange the carbomethoxy group for hydroxyl again.

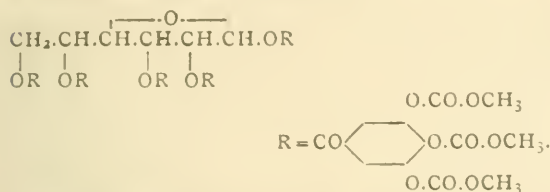
It is obvious that under these circumstances gallic acid would yield a tricarbomethoxy derivative—



which, when treated with phosphorus chloride, would yield the corresponding acid chloride. This chloride was finally treated with *d*-glucose in dry chloroform solution,

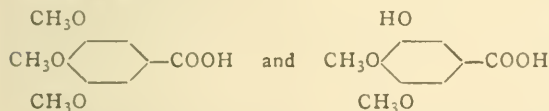
* Address before the Eastern New York Section of the American Chemical Society, Schenectady, 1914. From the *Journal of Industrial and Engineering Chemistry*, vi., No. 6

quinoline being introduced for the purpose of taking up the hydrochloric acid formed. The product was a pentatricarbomethoxy-gallate of glucose—

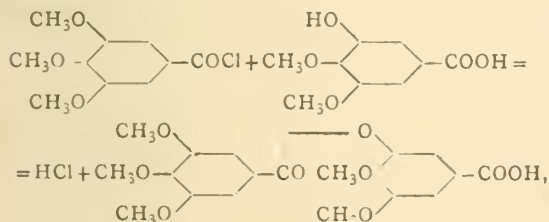


It was carefully saponified by means of a small excess of alkali dissolved in aqueous acetone. Under these circumstances the carbomethoxy groups were split off at ordinary temperature and the pentagallate of glucose was isolated. The similarity of this substance to ordinary tannin was striking. The only difference was in the rotatory power and the quantity of gallic acid formed by hydrolysis. Like tannin, the substance is amorphous, and it cannot be stated with certainty that it is perfectly homogeneous. Emil Fischer believes that there are probably at least two isomers present which stand to each other in the same relation as α - and β -glucose. This condition of things is certain in the case of glucose pentabenzoate.

The next step was the preparation of methylotannin, which proved easier to carry out than the synthesis of tannin itself. Herzig (*Ber.*, 1905, xxxviii., 989; *Monatshefte*, 1909, xxx., 543) had already prepared this substance by the action of diazomethane upon tannin, and had obtained, by hydrolysis, trimethylgallic acid and unsymmetrical *m.p.*-dimethylgallic acid.



These facts suggest that tannin might be an ester of glucose with five molecules of *m*-digallic acid. The synthesis was carried on much as before. Trimethylgalloyl chloride was first combined with *m.p.*-dimethylgallic acid—



and this, in its turn, changed to its chloride and combined with *d*-glucose. The product was strikingly similar to that of Herzig, but there remains, of course, the same doubt as to its perfect homogeneity as in the other case.

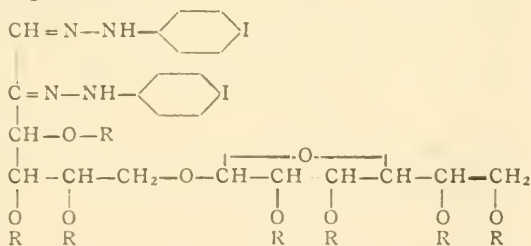
The success of these experiments seemed to warrant an attempt to prepare tannin itself: *m*-digallic acid, which had previously been synthesised, was changed to the carbomethoxy compound as in the simpler case of ordinary gallic acid, but the product was found to be amorphous, and the same is true of the chloride which is prepared from it. Finally, the combination with sugar took place only with difficulty and the synthesis cannot be regarded as successful. The essential nature of the tannins seems, however, to have been definitely settled by the investigation and we can be confident that the structure of tannin is typified by the penta-gallate of glucose. It is still possible, of course, that tannins from different sources have not exactly the same composition, and that any given sample of tannin is not homogeneous. It is also

possible that the *d*-glucose is not ready formed in the molecule, but that there exists instead some polysaccharide which gives *d*-glucose upon hydrolysis.

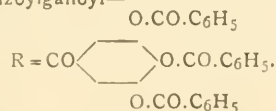
The investigation was continued by combining gallic and other hydroxy acids with other sugars and polyatomic alcohols, and a variety of substances were thus prepared which showed the chief tannin characteristics. Doubtless the study of compounds of this class will be of considerable value to plant physiology, since it is very likely that the plant builds up such substances as a means of neutralising acids by esterification. Some practical results may also be expected, since small quantities of tannin-like substances have a marked influence upon the taste of such articles of food as tea, coffee, and sweet fruits. It is, therefore, possible that synthetic materials of this type may find use as flavouring materials.

An interesting result of the investigation is to be found in the fact that syntheses of this kind lead naturally to products of extremely high molecular weight. In this property they surpass even the highest polypeptides. Emil Fischer expects to carry investigations of this sort further, believing that it is the duty of the Organic Chemist to build up as large molecules as possible, while the modern physicist is constantly dissecting the atom into smaller and smaller units.

By combining tribenzoylgallol chloride with the *p*-iodophenylsazone of maltose, Emil Fischer was able to prepare a substance of the formula $\text{C}_{220}\text{H}_{142}\text{O}_{58}\text{N}_4\text{I}_2$ and molecular weight 4021. This substance has the highest molecular weight of any organic compound which has yet been prepared by synthesis. Its graphic formula is given below—



and the only explanation necessary is that the radical R signifies tribenzoylgallol—



It is interesting to note that this substance follows the laws of Raoult very well. Determinations of the molecular weight by the freezing-point method, in bromoform, yielded numerical results which are surprisingly good when the magnitude of the molecule is taken into consideration.

This investigation has not led to the production of any substances which are sufficiently cheap to be of use to the tanner as a substitute for his extracts, but there has been brought upon the market within the last few months a laboratory product which is a promising substitute for tannin, and which is said by those in the trade to give good results and shorten the time required for tannage. This is the so-called "Neradol" of Stiasny (*Collegium*, 1913, 142). It is prepared by treating phenol with sulphuric acid and adding formaldehyde in the proportion of one molecule of formaldehyde to two of phenol. This method of preparation suggests the well-known Baekelite, but the product differs from the latter in being soluble in water. It enters the pores of the hide readily, and when used as a preliminary treatment increases the velocity of tannage by other materials. It also produces leathers of good quality and light colour.

MOLECULAR WEIGHT OF SODIUM CARBONATE AND THE ATOMIC WEIGHT OF CARBON REFERRED TO SILVER AND BROMINE.*

By THEODORE W. RICHARDS and CHARLES R. HOOVER

(Concluded from p. 7.)

The Solution and Quantitative Neutralisation of the Sodium Carbonate.

HAVING been carefully weighed in the weighing bottle containing dry air, into which it was transferred in the bottling apparatus, the sodium carbonate was now dissolved and neutralised in pure dilute hydrobromic acid. This solution was provided in carefully weighed quantity, almost exactly necessary to neutralise about 5 grms. of sodium carbonate, the amount usually employed in a determination. Because the method of dealing with this standard acid solution was somewhat unusual, a brief description is fitting.

Specialty designed weighing burettes containing the desired quantity of acid solution (about 200 cc.) were employed to weigh it. A large amount of the solution had been prepared shortly beforehand and preserved in a bottle of resistant glass, from which it could be removed by a paraffin coated and lined glass syphon. Air was admitted to the bottle after passing through a U tube containing a solution of the same nature and concentration as that in the bottle. When the burette was to be filled, after thorough agitation of the solution (which was at room temperature), a portion was drawn off sufficient to wash the interior of the syphon, the last of this being added to the U-tube, replacing the solution which had previously been in the tube. Small portions of the acid solution were now run into the dry weighing burette, which was closed and gently shaken until it was thoroughly rinsed, and filled with the vapour of the solution. The burette was then filled, with the syphon-tip inserted far into its interior, to avoid evaporation. Subsequently the burette was carefully wiped with a slightly damp, perfectly clean linen cloth, and thereafter touched only with platinum forceps or linen cloth. After standing with the upper cock nearly closed in the balance-case for one hour, the weight was taken by substitution, using a precisely similar, partly filled companion burette as substituting tare. Before filling a burette the bottle containing the acid solution had been placed for some hours near the balance, so that long waiting was unnecessary.

The required amount of solution was next removed from the burette and placed in the bowl of a very large platinum retort, the graduations upon the burette allowing one to determine to within 0.1 grm. when the required weight had been removed. The burette was then returned to the balance case, and in not less than an hour its weight was determined as before. It was found that three such complete manipulation could be carried out in succession, each consisting of weighing after one hour in the balance case, removing burette to the titration room, replacing and removing the tip from the burette outlet, and re-weighing, without any change in weight exceeding a mgrm. As a rule of course in actual analysis only one such operation was carried out.

As will be detailed, the concentration of this solution was exactly determined by reference to silver, the solution being weighed out for this purpose in successive portions, just as for the neutralisation, but in order to not interrupt the narrative the discussion of the neutralisation will be continued.

As already stated, the exactly weighed acid solution was placed for the neutralisation of the sodium carbonate into the body of a large platinum retort, very kindly given by Prof. J. M. Crafts, and the weighed boat with the fused carbonate was carefully lowered into the solution. The

tightly fitting cover was then placed on the retort with the condenser tube attached, and the whole was set aside for some hours, usually over night. The condenser tube was packed with scraps of platinum foil to serve as baffles, and the lower end placed into a gold flask, which served to collect any solution projected in minute drops during the evolution of gas. When the fused salt was completely dissolved, the retort, with condenser attached, was very gradually warmed during several hours, until at last boiling commenced. The supply of heat was then decreased, and the condenser tube and gold flask were removed and rinsed into the retort, which was now covered, placed in an electric oven or bath, and warmed, while very pure air was passed in through a hard glass tube bent to deliver the air just above the surface of the liquid. During the evaporation thus conducted the temperature of the oven was maintained at a point slightly above 100°, actual ebullition being prevented by the cooling effect of rapid vaporisation. When the volume of the solution had been reduced to about one-half the heating was discontinued, and the retort was cooled in a current of pure air. Methyl red was added to the cool liquid as indicator, showing in general an alkaline reaction. This outcome had been arranged beforehand in weighing the acid, in order to prevent possible loss of bromine during the evaporation.

The next step was the completion of the titration, using a very dilute solution (approximately 0.01 N) of hydrobromic acid, which had been prepared by diluting the more concentrated acid and standardised by titration against dilute carbonate-free sodium hydroxide and by precipitating with silver nitrate. This dilute standard solution was weighed in a smaller set of weighing burettes, and added drop by drop to the solution in the retort. For this purpose the platinum cover of the retort had been removed and a glass plate having two small openings put in its place; through one of these openings the tube admitting a rapid stream of pure air was passed, while the other served to admit the tip of the weighing burette. When a distinct acid reaction was attained the burette was removed, and if the amount added was comparatively large the burette was weighed and emptied. If, however, the amount added was small, the burette was placed in the balance case and removed for a second addition after the carbonic acid formed by the previous addition had been expelled. As with the stronger solution, we found that it was possible, using care not to touch the burette with the hands and allowing but little change in the temperature of the room, to work with the burette for several hours without producing a significant change in the weight.

The expelling of the carbon dioxide produced by the addition of dilute acid was usually complete within one-half hour at a temperature just below boiling, with a rapid current of pure air passing over the solution. In no case was there a change in the depth of indicator colour after the solution had been heated for one hour. Consequently this was the usual time of heating the retort, after the addition of a portion of dilute acid. Experience taught that a certain depth of pink was required in order that the solution would be left neutral when the excess of carbonic acid had been expelled, and this helped materially to shorten the tedious process of reaching the end-point by this method. In short, this method of adding successive small portions of very dilute hydrobromic acid was continued until an end-point slightly on the acid side of exact neutrality was reached, which remained unchanged when cold after at least an hour's heating, frequently with slight boiling during the last stage. It was thought for a time in the preliminary work that the end-point might be determined in a hot solution, but the action of the indicator is less reliable at the higher temperature under the conditions concerned, and the difficulty of manipulating the hot solution, especially because of the obstruction of clear vision by the drops condensed on the glass plate, caused us to cool the liquid in order to attain the accuracy demanded.

In two titrations an equivalent amount of *p*-nitrophenol was added to the methyl red. This mixture is very well

* Contribution from the Wolcott Gibbs Memorial Laboratory of Harvard College. From the *Journal of the American Chemical Society*, xxvii, No. 1.

adapted for the titration of all strong acids and bases, working from either acid or alkaline solution. With a concentration of ionised hydrogen of 10^{-8} the mixture shows a distinct yellow colour, at 10^{-7} the colour is a very faint greenish yellow, almost colourless, while at 10^{-6} the pink of methyl red appears. In hot solution it is less reliable than methyl red alone, tending to make the solution appear too alkaline, but it resumes its normal reaction when cooled to room temperature. It cannot be depended upon in solutions containing more than 15 or 20 per cent of dissolved substance, especially in sulphate solutions. The weight of the indicator substance required is very small—from 0.05 to 0.08 mgrm. of methyl red sufficing for 100 cc. solution, and the amount transformed, when a distinct pink is noticed, is not more than one-half this, as determined by Noyes's method of superimposing solutions. Hence, considering the high molecular weight of the indicator, it is certain that no weighable amount of acid or base was required to combine with the indicator. Confirming this conclusion it was found that one drop of 0.01 *N* solution of acid containing 0.03 mgrm. of bromine would change the reaction from distinct alkaline to distinct acid. For yellow or red indicators the eye is much more sensitive to a small change in colour when the solution is placed in the bottom of a platinum vessel than when it is contained in glass or porcelain. The methyl red, of course, gives the final evidence as to the true neutral point, but for rapid work the mixture of indicators can be used to advantage, since it gives more warning of approach to the end-point from either acid or basic side.

After the sodium carbonate had been neutralised with hydrobromic acid, the sodium bromide solution resulting was quantitatively transferred to a glass-stoppered precipitating flask and diluted, and the calculated quantity of silver, having been dissolved with great precaution in nitric acid, was added. The exact end-point of the precipitation was determined in the usual nephelometric manner.

The above described method of reaching the end-point by gradual addition of very dilute hydrobromic acid was employed in five of the six determinations. In the third experiment (No. 11 in Table II.) a very slight excess of hydrobromic acid was added during the first operation. This excess was titrated very carefully with dilute carbonate-free sodium hydroxide solution, which had been standardised against both dilute and concentrated hydrobromic acid solutions. The fact that in this experiment essentially the same quantity of hydrobromic acid was used as in the others suggests that the danger of loss of bromine during evaporation from an acidifying liquid is very slight.

Besides thus finding the weight of silver needed to precipitate the ionised bromine balancing the ionised sodium from the sodium carbonate, we made separate determinations of the amount of silver needed to precipitate given weights of the same solution of hydrobromic acid, and also in four cases weighed the silver bromide which resulted. By giving the exact weights of silver and of bromine corresponding to a given weight of the hydrobromic acid solution, these determinations made it possible to compute, in a way entirely independent of the other determinations, the amount of silver and silver bromide corresponding to given weights of the solution used for neutralising various portions of sodium carbonate, it being assumed, of course, that the neutralisation was correctly performed. The agreement of these results with the others showed that—at least as far as the determination of the bromine was concerned—the earlier results were trustworthy. They showed, moreover, that no significant amount of hydrobromic acid was lost on the average during neutralisation and evaporation, for the silver analyses were made in one case after evaporation and in the other case without any such treatment. Several of these analyses were made in the midst of the earlier series; indeed the intention was to make them alternately.

The question having arisen as to the possible action of the dilute hydrobromic acid on the resistant bottle in

which it was kept, experiments were instituted on purpose to test this point, for such action would have had a highly deleterious effect upon the result, introducing sodium bromide from a foreign source. The final distillation of the acid had occurred on March 20, 1913, and not long afterwards the solution was made up in its final form. All the analyses were concluded before May 10, an interval of less than seven weeks. Six months after that, the acid having remained in the same bottle, two portions of 60 grms. each were separately evaporated in a quartz dish, and the barely visible trace of residue was dissolved in water, transferred to a small platinum crucible, dried and weighed. In each case the residue weighed only 0.1 mgrm., and the solution in water was found in the nephelometer to contain an amount of soluble bromide equivalent to 0.04 mgrm. sodium bromide. The amount of sodium bromide formed from the flask during the first six weeks in question must, therefore, have amounted to less than 0.01 mgrm., a negligible quantity. It should be stated that this flask had previously been used for dilute hydrobromic acid for several years; probably a new bottle would not have yielded so satisfactory a result.

Incidentally, in order to reduce the results to the vacuum standard, the specific gravity of sodium carbonate was determined by weighing it in a pycnometer under toluene, which had been found in two closely agreeing experiments to have a density at 20° of 0.8661 referred to water at 4°. Thus, 9.7256 grms. and 5.62691 grms. of salt were found to displace 3.32581 grms. and 1.92439 grms. of toluene respectively at the same temperature. The two values for the density of the salt were, therefore, 2.3327 and 2.5325 respectively. This value is distinctly higher than the results of other experimenters. For example, Schroeder found values ranging between 2.43 and 2.51 ("Landolt-Börnstein," 1912, 180). The difference is doubtless due to the more compact condition of our fused material and the absence of air held within the pores of the substance.

Table I. reports the weights of silver and silver bromide obtained from given weights of the standard hydrobromic acid solution. All the analyses are recorded, excepting two which met with accidents and could not be brought to completion.

TABLE I.—Analyses of Hydrobromic Acid Solution.

No. expt.	Sample of silver.	Weight of HBr sol. (in vac.).	Weight Ag (in vac.).	Weight AgBr (in vac.).	Weight Ag per 100.000 grms. solution.	Weight AgBr per 100.000 grms. solution.
1	—	205.192	—	17.05459	—	8.3115
2	—	199.157	—	16.55319	—	8.3116
3	I.	212.457	10.14346	17.65772	4.7743	8.3112
4	II.	211.335	10.08975	17.56405	4.7742	8.3111
6	III.	201.663	9.62812	—	4.7744	—
8	II.	198.356	9.47115	—	4.7748	—
Average ..					4.77442	8.31135

Thus, 100.000 grms. of silver bromide are found (from the two averages) to correspond to 57.4446 grms. of silver. Baxter (*Proc. Am. Acad.*, 1906, xlii., 210) found 57.4453 grms.—very nearly the same figure. If we assume Baxter's value (because determined in a simpler way) to be correct, our average—4.77442 grms. of silver—corresponds to 8.31125 grms. of silver bromide, or very nearly the result (8.31135) found directly, as given above. The average between these averages, or 8.31130 grms. of silver bromide, must represent very nearly the true amount of precipitated halide to be obtained from 100.000 grms. of the hydrobromic acid solution. This weight of silver bromide corresponds to 3.5815 grms. of hydrobromic acid gas—a figure which gives the percentage composition of the acid, enabling us to know the density of the solution and apply accurately the large correction to the vacuum standard in weighing.

Evidently the concentration of the hydrobromic acid remained essentially constant during the time concerned.

Table II. records the weights of hydrobromic acid solution taken for the neutralisation of the several samples of sodium carbonate, the weights of these samples, the weights of the salt corresponding to 100.000 grms. of acid solution, and finally the molecular weight of sodium carbonate and the atomic weight of carbon computed from these results (with the help of the weight of silver bromide corresponding to the hydrobromic acid, as computed from Table I) if silver is 107.88, bromine 79.916, and sodium 22.995. Incidentally, the total weight of the dilute acid would have been capable of precipitating $1254.946 \times 0.053113 = 104.3023$ grms. of silver bromide; hence we may write the proportion—

$$104.3023 : 29.43501 = 2 \times 187.796 : 105.995 = \text{Na}_2\text{CO}_3.$$

TABLE II.—*Molecular Weight of Sodium Carbonate. First Method.*

N. of expt	Weight of HBr sol (in vac)	Weight of Na_2CO_3 (in vac)	Weight of Na_2CO_3 per 100.000 grms. solution.	Calc. mol. wt Na_2CO_3 (if AgBr = 187.796).	Calc. atomic wt. carbon (if Na = 22.995).
9	202.744	4.75555	2.34559	105.998	12.008
10	204.673	4.80081	2.34560	105.999	12.009
11	208.457	4.88936	2.34550	105.994	12.004
12	240.119	5.63157	2.34533	105.987	11.997
13	191.646	4.49516	2.34555	105.996	12.006
14	207.307	4.86256	2.34559	105.998	12.008
Sum	1254.946	29.43501	Av. 2.34553	105.995	12.005

The average value for carbon is seen to be 12.005. Considering the circumstances, the agreement of the individual results is as good as could be expected. Before discussing the outcome, another series of more directly obtainable data—namely, the weights of silver actually needed for the precipitation of the exactly neutralised sodium bromide made from these specimens of sodium carbonate—will be recorded. In Table III. these several weights of silver are entered in the fifth column, the quality of the silver being indicated by the numerals in the third, which correspond to the various samples already described. The next to the last column, again, contains the computed molecular weight of sodium carbonate, and the last column the atomic weight of carbon, calculated on the same basis as the values recorded in Table II.

TABLE III.—*Molecular Weight of Sodium Carbonate. Second Method, by More Direct Reference to Silver.*

N. of expt	Sample of Na_2CO_3	Sample Ag.	Weight of Na_2CO_3 (in vac.)	Weight of Ag (in vac.)	Mol. wt. Na_2CO_3 if Ag = 107.88	Atomic carbon if Na = 22.995.
15 (A)	I.	4.75555	9.68023	105.995	12.005	
16 (A)	II.	4.80081	9.77222	105.997	12.007	
17 (B)	II.	4.88936	9.95301	105.991	12.001	
18 (B)	III.	5.63157	11.46316	105.998	12.008	
19 (C)	III.	4.49516	9.15003	105.997	12.007	
20 (C)	II.	4.86256	9.89811	105.994	12.004	
Sum	..	29.43501	59.91676	Av. 105.995	12.005	

In brief, it appears that the atomic weight of carbon, calculated from the weight of hydrobromic acid taken, is exactly identical with that found from the directly determined weight of silver needed to precipitate the acid required for neutralising the carbonate, each being 12.005 on the basis given, if silver equals 107.88. On the other hand, if Ag=107.871 (a contingency not impossible),

carbon becomes exactly 12.000. The probable error of the average of the entire series of twelve values, if each is given equal weight, is less than 0.001 in the atomic weight of carbon. This is less than 0.003 per cent in the weight of the sodium carbonate, or less than 0.2 mgrm. in the actual weighing of this salt. The results, then, are about of the order of accuracy of much of the modern careful work on atomic weights.

The final limits for carbon—viz., 12.000 to 12.005, according to the value for silver chosen—are near that found for carbon in other ways. The range is indeed as small as the limit of accuracy of the usually accepted data concerning either carbon or silver. That in this entirely different way the old value for carbon should be verified is a highly comforting and reassuring circumstance. It inspires confidence in the accuracy of all the processes concerned, both in the new work on halogen compounds and the older work on carbon, because the single method may be always open to the suspicion that a small constant source of error may have been inadvertently overlooked, the value of such confirmatory evidence is great.

The work could not have been carried out at this time without a generous subsidy from the Carnegie Institution of Washington, which is hereby gratefully acknowledged.

Summary.

A new method of determining the molecular weight of sodium carbonate, and therefore the atomic weight of carbon, is described, depending upon the neutralisation of pure, fused, weighed sodium carbonate by hydrobromic acid, and the precipitation of the bromine both in the resulting sodium bromide and other portions of original solution by means of pure silver. It was found that 29.43501 grms. of sodium carbonate were equivalent to 59.91676 grms. of silver, and also to a weight of dilute hydrobromic acid which had been found in other tests to be capable of precipitating 104.3023 grms. of silver bromide. From these results, if silver equals 107.88, sodium carbonate becomes 105.995 and carbon 12.005, and if silver equals 108.87 and sodium 22.993, carbon becomes 12.000. These limits in both cases are about the possible range of accuracy of the earlier determinations by various methods; hence the present work, by connecting the various ratios in a new way, shows the consistency of a great variety of earlier work.

THE MANUFACTURE OF ACID PHOSPHATE.*

By WM. H. WAGGAMAN, Scientist in Fertiliser Investigations

(Concluded from p. 10).

SUMMARY.

THE general procedure followed in making acid phosphate involves numerous details of great economic importance which are not thoroughly understood.

The raw phosphatic materials which have been used in the acid phosphate industry are bone, guano, apatite, and phosphate rock. Of these substances the last-named has practically displaced the others as a source of phosphoric acid.

The process of making acid phosphate was devised in order to produce phosphoric acid in a soluble, or so-called "available," condition; this is done by the action of sulphuric acid on tribasic phosphates whereby less basic and more soluble phosphates are produced.

A knowledge of the composition of the raw materials is of the greatest importance in the manufacture of acid phosphate, since not only the phosphate of lime but all the impurities contained in the rock are acted upon by

* Bulletin 144, U.S. Department of Agriculture, Bureau of Soils.

sulphuric acid and influence the composition and physical condition of the finished product.

Much phosphate rock contains organic matter which consumes a certain amount of sulphuric acid, but owing to the various forms in which this material occurs it is almost impossible to determine except by actual trial the quantity of acid required to decompose it.

Silica is acted upon only indirectly by sulphuric acid.

Calcium fluoride, which is present in nearly all phosphate rock, is acted upon by sulphuric acid, resulting in the formation of gaseous hydrofluoric acid. This gas in turn acts upon silica and silicates, producing silicon tetrafluoride. The silicon tetrafluoride is decomposed by water, forming hydrofluosilicic acid and silica. The presence of fluorides is objectionable because of the obnoxious fumes evolved in treating with acid; otherwise this impurity is not objectionable.

Compounds of iron and aluminium are the most dreaded of the impurities occurring in phosphate rock. These elements when present in small quantities are very apt to cause a certain amount of reversion to take place, and when present in large quantities may render the product sticky and unfit for use. By careful handling, however, phosphates high in iron and aluminium compounds may be made to produce high-grade acid phosphate.

Carbonate of lime, which is present in nearly all phosphate rock, is a rather desirable impurity when the quantity is not excessive. The decomposition of this compound by sulphuric acid is attended with considerable heat which promotes chemical reaction between the more slowly acting substances in the mass; moreover, the calcium sulphate produced therefrom acts as a drier for the acidphosphate.

In the manufacture of acid phosphate the rock is first ground to pass a 60-mesh sieve, and then mixed with an equal weight (approximately) of "chamber acid." The quantity, strength, and temperature of acid used have an important influence on the quality of the product.

After thorough mixing in a cast-iron pan the material is discharged into a "den" just below the mixer or into a car which takes it to a shed and dumps it on a pile. When the "den" system is used the reactions take place rapidly, and the product can be dug out in twenty-four to thirty-six hours, practically ready for shipment. The method of emptying the "dens" by hand, however, is attended with some risk owing to the poisonous nature of the fumes evolved from the freshly-made acid phosphate, and to the danger of large masses of the material falling on the labourers.

In the "open-dump" system the acid phosphate requires a long time to reach its maximum availability, and unless it is properly made may never be fit for use.

The storing of acid phosphate in large piles for protracted periods sometimes causes reversion owing to the pressure on the material in the lower part of the pile; this pressure also tends to compact the material. The storing of well-made acid phosphate in medium sized piles, however, should cause no ill effects.

Properly made acid phosphate should require no artificial drying, since the calcium sulphate formed in the process takes up the water to form gypsum. It is nearly always necessary, however, to disintegrate and screen the material before shipping. This is often done by simply throwing the product upon inclined screens, but sometimes disintegrating machines must be employed.

Acid phosphate is sold on the basis of its so-called available phosphoric acid, and has a value of 40 to 56 cents per unit. The marketed product contains from 14 to 21 per cent phosphoric acid, depending on the raw material used in its manufacture.

Double acid phosphate is made by treating phosphate rock with sufficient diluted sulphuric acid to produce free phosphoric acid, and then using the phosphoric acid thus obtained to decompose a fresh batch of rock. The final product contains from two to three times as much phosphoric acid as ordinary acid phosphate, and is very useful in the making of concentrated fertilisers.

THE CYANIDE PROCESS.*

By FRANK S. WASHBURN.

THE fixation of atmospheric nitrogen has had commercial application for the past ten years. During this period different types of processes have been conceived; four, the Serpek, Haber, Arc, and Cyanamid, have seriously attempted commercial exploitation; two, the "Arc" and "Cyanamid" processes, have proved to be commercially practicable in the broad sense. Of these two the latter may justly claim to be of great economic importance to the world because the unit of fixed nitrogen in its first product is capable of being more cheaply produced than by any other present-known process, and because this first product has a direct and valuable use of itself and constitutes the raw material for a varied and important line of derivatives into which, for the most part, it can be cheaply transformed.

The annual productive capacity of the existing plants employing the "Arc" and "Cyanamid" processes is between 90,000 and 100,000 net tons of fixed nitrogen, which, at the normal average value of the product at the factory door, represents 25,000,000 dols. This is divided in the ratio of two-thirds to "Cyanamid" and one-third to the "Arc" process. The American Cyanamid Company's factory at Niagara Falls, Canada, has alone a capacity in fixed nitrogen approximately half as great as the total world's installed capacity by the "Arc" processes.

More than three thousand technical articles dealing with almost every conceivable phase of nitrogen fixation have appeared in different languages. The patents applying to the subject in all its branches number into the thousands. So far as the author of this paper knows, nothing has appeared in the nature of a differentiation of processes based on the economics of the world demand for nitrogen. It is only for a limited developmental period that the theoretical, technical advantages and limitations of related processes constitute a practical basis for hazarding opinions as to their ultimate commercial value. It is also true that until an art has had some years of commercial application it is impossible to analyse and draw sound conclusions from the economics of the situation, the final arbiter in determining the social value of any process.

The art of atmospheric nitrogen fixation is now old enough to enable one to see the economic aspects of the case, and therefore, in casting about to determine what part of this vast subject to deal with in this paper, the author thought it would be of interest and possibly of value to treat herein the broad commercial outlook for the various fixation processes, and in order to limit the matter to conditions more or less well known to all of us, conditions on the North American continent, for the most part, will be the only ones considered.

Two nitrogenous compounds, nitrate of soda and sulphate of ammonia, constitute in value 80 to 85 per cent of the total raw nitrogen compounds produced throughout the world. The value of their combined production in 1913 was between 190,000,000 dols. and 200,000,000 dols. It is estimated that 80 per cent went to agriculture, corresponding to an annual per capita tax on the 600,000,000 inhabitants of the earth of 33 cents.

Nitrogen has four main uses: as an agricultural fertiliser, as nitric acid and derivatives therefrom, as ammonia, and in dyes and various other chemical compounds. Measured in the quantity of contained nitrogen, and in view of the restricted opportunities in the United States for immediately developing the chemical and dye industries on a large scale, we need consider as bearing decisively on atmospheric nitrogen fixation processes only the three first-mentioned uses, namely, for crop fertiliser, for nitric acid and its derivatives, and for ammonia as such.

The farmers' purchases in nitrogen used east of the Mississippi River last year approximated 75,000,000 dols.

* From the *Chemical Engineer*, xxi., No. 5.

More than 90 per cent of fertiliser nitrogen is in the form of ammonia. The normal annual consumption of nitric acid in the same region is about 7,000,000 dols. The price paid per unit of nitrogen is about the same for each, and the percentage annual increment of consumption is about 10 per cent in each case. However, the importance of the fertiliser field in comparison with the nitric acid field, in their bearing on the fixation of atmospheric nitrogen, is not fully nor even approximately measured by this ratio of ten to one.

The use of nitric acid is along established lines looking comfortably to the future for a steady growth, with no serious limitations hampering modest development and no great unsatisfied human need demanding great development. It is essentially a small business as great industries go. The fertiliser industry has a very different significance. The population of the United States from 1900 to 1910 grew from 76,000,000 to 92,000,000, an increase of 21 per cent. Crop production increased 10 per cent in the same period. Exports of wheat and flour decreased from 31 per cent of their production to 13 per cent. The importation of foodstuffs and live animals practically doubled, while imported manufactured foodstuffs more than doubled. Beef cattle production fell off 32 per cent as the population increased 21 per cent. These figures are strikingly reflected in the increased cost of foodstuffs, which from 1896 to 1912 amounted to 80 per cent in the United States, while the general advancement in the cost of living during this period was 59 per cent in the United States, 40 per cent in England, and 40 to 45 per cent in continental Europe.

These facts point to the necessity of increasing crop yields without additional labour—and that defines fertiliser. European yields per acre cultivated are 50 to 100 per cent greater than American yields. The use of fertiliser in Europe, per acre cultivated, is enormously greater than in America. The average increase in yield in Germany for the past twenty years has been approximately 60 per cent, in the United States 20 per cent. Abroad this increase is attributed to intensive farming, better selection of seed, the rotation of crops, and, to the extent of 50 to 70 per cent of the increase, to the use of commercial fertilisers.

The farmers' purchases of fertiliser in the United States last year in nitrogen and phosphorous constituents (later it will be shown why both are here included) was approximately 150,000,000 dols. Were the cultivated lands east of the Mississippi to receive for each of two years out of every three the quantity of fertiliser normally used per acre each year in Germany, the bill would have been approximately 1,600,000,000 dols., or ten times as great as the actual expenditure. The very limited use of fertilisers in the United States does not arise from the possibility that fertilisers do not pay. Indiana experiments, conducted in ten counties, produced an average increase of 11.6 bushels of wheat per acre, valued at 11.60 dols., for an expenditure of 3.67 dols. An instance of a very low return in the use of fertilisers is an unpublished record of thirty seven experiments in Illinois in 1913, showing an average increase of 5.2 bushels of wheat, valued at double what the fertiliser cost.

The fertiliser industry to-day suffers many handicaps. These originate in part from the farmer's limited capital for properly conducting his business, his lack of knowledge which closes to him what would otherwise be avenues of advancement and prosperity, and in part also from the fact that there is no vital, broadcast propaganda and educational bureau conducted by the fertiliser industry itself.

The greatest handicap is possibly in the material used. The industry is carried on by collecting at a great number of places throughout the agricultural regions east of the Mississippi a great variety of materials, each containing some one of the so-called plant foods, namely, nitrogen, phosphorus, and potash, the last representing only about 10 per cent of the total. For the most part these materials are low in fertilising value, and when mixed in a manner

to include the low as well as the high-priced materials, there results of necessity a product of which 85 to 90 per cent is useless dead weight, only the small remainder having fertiliser value. Forty per cent of the annual fertiliser product in value is in the nitrogen constituent drawn from materials that are either by-products or wastes, such as sulphate of ammonia, slaughter-house refuse, fish scrap, vegetable refuse, waste of sugar works and distilleries, hair, leather, wool, hoofs, and horns. The phosphoric acid constituent is secured from acid phosphate analysing from 14 to 16 per cent P_2O_5 , and as a general rule constituting one-half of the complete fertiliser mixture. Few of these raw materials in the broad sense are satisfactory. They are borne with because up to the present time there are no others commercially available. They pay the uttermost limit in the way of transportation charges to the point of their preparation, and after being mixed they bear a further great transportation burden to the consumer's railway station. There is a relatively large expense for mixing, storing, drying, bagging, and selling. After the farmer has received his goods at the railway station, he must haul over spring roads, often almost impassable, 1000 pounds of material in order to get 150 pounds of plant food. It is one of the recognised, recurring, contributing causes for small crops, particularly in the South, that the roads are so bad in the spring, due to rains, that farmers cannot haul the necessary amount of fertiliser.

Notwithstanding the consumer pays for nondescript materials, requiring only to be mixed in the crudest manner, a price 60 per cent greater than their spot value, the fertiliser industry as a whole, which prepares and sells the product, is conducted without measurable profit.

Unless revolutionary developments in some vital respect come to the aid of this great industry in the United States, any marked improvement is impracticable. It would appear, for reasons already set forth, that possibly the matter of greatest economic importance in the United States to-day is that conditions shall be brought about by which the farmer will use a vastly greater quantity of fertiliser than is now used. We believe the most important single contribution to this end would be a high-grade chemical salt containing nitrogen and phosphorus, well balanced and in large percentages, and possessing in a high degree the many requisites of a good fertiliser, such as being non-hygroscopic, non-toxic, finely granular in form, non-leachable in the soil, and readily convertible by nature's forces into the organism of the plant. The process for the fixation of atmospheric nitrogen that will contribute the nitrogen content to such a fertiliser compound to the greatest net advantage may be justly viewed as the most important, not only to society, but also therefore to those who exploit it.

Discussions of the ultimate commercial superiority of a favourite process and the consequent complete annihilation of every other have been almost interminable. These have proceeded apart from any broad conception of time, place, the demands of mankind, or the quantitative application of the product. They generally take the form of rival claims for cheapness in the cost of production, and this without much reference as to whether the unit cost applied to a form of nitrogen for which there was any particular or large demand, and without reference to whether the product was to be produced at a place and in a form enabling it to be transported to the consumer.

The Serpek process was discussed by volunteer adherents without knowledge that per unit of nitrogen fixed the necessary expenditure of heat energy from electricity alone is as great as the total electric energy consumption in cyanamid. Therefore, no suspicion was aroused that possibly nature had not placed the necessary raw material, bauxite, within practically shipping distance of equally necessary cheap water powers. The limitations of the by-product, upon which the commercial possibilities of the process depend, were not questioned either as to the

difficulties in converting it to commercial aluminium or as to the relation of its volume to the market demand for the metal.

The Haber process has been taken by the public for granted as one practicable of universal application because of its larger though single use by a great concern of brilliant accomplishments in the commercial chemical world. The public does not know of the pressing problem of disposing of great quantities of sulphuric acid, and the single problem involved of how, under the local conditions, to devise the cheapest possible means of providing the requisite ammonia for using the acid in sulphate of ammonia. The electric energy necessary to the process is generally considered negligible, and yet a proposal to establish a plant close to New York involved, at the necessary power cost in that vicinity, as great an expense for electric power as the total power cost for cyanamid in an available site then under consideration for that process.

Air nitrogen fixation processes divide themselves into two broad classes, namely, those that come in at the nitric acid end, and those that come in at the other extreme, the ammonia end. There is no expectation that the various "arc" processes producing nitric acid will ever have employment in the production of ammonia compounds, for the sufficient reason that there is no prospect of ever being able to commercially convert nitric acid to ammonia. Therefore, the best that can be said of the "arc" processes is that they may be able, by reason of having nitric acid as their first product, to occupy exclusively the field for the production of nitric acid. We have already seen that this field is not only relatively but absolutely a limited one for the present, as it is prospectively for the future.

The "ammonia" processes are not ready to admit, however, that there is an insurmountable barrier separating them from the nitric acid field. A tried, thoroughly workable, commercial plant for the oxidation of ammonia into nitric acid is not yet complete and in entirely satisfactory operation, but, on the other hand, the various steps necessary to the operation of such a plant have been separately brought to such stages of development as to leave no doubt in the minds of the experienced men who have worked upon the problem of the ultimate complete commercial practicability of carrying the ammonia processes for the fixation of atmospheric nitrogen through to the nitric acid producing stage.

A powerful factor operating as a disadvantage in the "arc" processes to the manufacture of nitric acid is the extraordinary difficulty of transporting the acid from the remote, cheaply developed water powers, very limited in number, where alone these processes can be employed, to the place of use for the acid, both sea and rail transportation being practically invariably necessary. This audience does not need to be told how serious a matter this is. The nitrate compounds made from acid produced by the "arc" processes have found no place as a fertiliser in this country. Nitrate of lime, even in the so-called basic form, is too strongly hygroscopic to permit its use alone or as part of a mixture to be used through the ordinary drills by which fertiliser is distributed to the soil in this country. Even if the physical form were entirely satisfactory, it could not satisfactorily have a very large place in fertiliser mixtures in this country because of its being too readily available in the soil and because the valuable form of fertiliser nitrogen is as ammonia and not as nitrate. We have seen furthermore that the fertiliser industry demands something more than a new nitrogenous material, however meritorious it may be, merely as an additional one to the many which now constitute a part of a complete fertiliser mixture.

For a time it was thought that the treatment of phosphate rock by nitric acid might possibly find a large place in the fertiliser world. Two decisively unfavourable and irremedial results have developed from this attempt; first, the product is excessively hygroscopic, the surface when

exposed taking up sufficient moisture to reduce the external parts to a molasses-like condition, and second, the content in plant food, approximately 11 per cent nitrogen and 14 per cent phosphoric acid, is markedly lower than that readily securable in the new commercial ammonium phosphate compounds resulting from the combining of ammonia and phosphoric acid. When carried to the monocalcic stage, thereby giving it the desired water solubility, the excess acid is of necessity so great that the crop is burned and destroyed. Much money has been spent on these efforts, which have always resulted in failure.

This brings us now to the consideration of the practicability of an ammonia-phosphoric acid compound for agricultural use. The mono-ammonium phosphate, containing theoretically 14.6 per cent of ammonia and 61.3 per cent of phosphoric acid (P_2O_5) and the di ammonium phosphate, containing theoretically 21.8 per cent of ammonia and 53.4 per cent of phosphoric acid, have been recognised by the scientific world for many years as fertilisers of extraordinary value, being in effect perfect materials, as they possess every qualification of a good fertiliser. The manufactured product made in this country has not developed any limitation. Under some circumstances, at least, the results in crop increase are greater per unit of ammonia and phosphoric acid than is securable from any other fertiliser or fertiliser compound, and the question has arisen whether this salt may not produce its result partially from the exercise of the same natural laws that apply to the action of manganese sulphate, for instance, in which there is a crop increase that cannot be attributed to the taking up by the plant of anything contained in the fertiliser. The effect may some day be safely attributed to the inducement that the salt has given to increased activity of the chlorophyll and thereby increased power of assimilation on the part of the plant.

The commercial ammonium phosphate product may be readily produced at will with varying proportions of ammonia and phosphoric acid, ranging from 13 and 47 to 21 and 46 per cent respectively. Thus it is that the plant food constituents of this single material, varying between 60 and 67 per cent, occupy the entire range of the usually desired relationship between ammonia and phosphoric acid. The phosphoric acid content of the commercial acid phosphate now used in agriculture, a product which, roughly speaking, results from pouring a ton of 52° sulphuric acid on a ton of rock containing 30 to 32 per cent P_2O_5 , contains about 14 to 16 per cent P_2O_5 . In value it constitutes about one-half the farmer's fertiliser bill in the United States each year. Whatever advantages a new kind of phosphoric-acid-containing material may have, it should be capable of being produced at a cost no greater than the per cent unit cost of phosphoric acid in acid phosphate.

Two methods of manufacturing ammonium phosphate compounds have been developed. One of these is in the proved commercial stage and can produce as cheaply, at least, as by acid phosphate. The other is in the advanced developmental stage and promises still cheaper production costs. The first is applicable wherever cheap sulphuric acid may be had, and the second, which employs the electric furnace in driving off phosphorus from the phosphate rock, is applicable only where there is cheap water power available.

When the problem is referred to the actual conditions existing on the North American continent, the most available process known for providing agriculture in a broad way with the ammonia constituent of an ammonium phosphate compound is the "cyanamid" process. Searching investigation and analysis, for four years, of prospective cyanamid manufacturing sites, covering the United States and Canada, has developed a state of facts establishing the practicability of placing ammonia at the disposal of agriculture and the arts in practically every place of large use in the United States, and cheaper and simpler than could be accomplished in any other way.

This may be done by shipment of cyanamid from a central point of manufacture to these various localities and its conversion there into ammonia.

These natural tendencies towards the "Cyanamid" process as the principal source for nitrogen supply might be turned aside, however, unless that material and its important derivatives, notably ammonia, could be produced and delivered to the consumer cheaper than by other means and through the employment of capital in such a manner as would induce the investment of money in the undertaking. This brings us then to a consideration of the costs of production applied to a distinctive set of conditions which correspond not only with all the important conditions surrounding the demand for and use of the product but also those which characterise an actual place of production and its geographical relation to the consumer.

There is properly a hesitancy on the part of any business enterprise to disclose actual costs. Such information is frequently made wrong use of, and the risk involved in making it public is wholly out of proportion to the gain. At the same time the author realises that without volunteering exact statements of comparative cost figures, open to confirmation or refutation, as the case may be, it is difficult to carry conviction to the hearer that one's conclusions are sound. The founders of the American Cyanamid Company have not from the beginning been wedded to any particular process for the fixation of atmospheric nitrogen. The aim and policy has been to conduct the company's activities and research work toward the end of developing a great nitrogen industry. It has investigated many processes with the conviction that it could not hope to have permanent and ultimate success except through the application of the best. Its research work in entirely new fields, and in the regular manufacture of its product, has been practically continuous from the day it first began commercial operations in 1910. It is therefore natural that those connected with the company should feel confident of their judgment on many matters bearing upon the relative merits and limitations of various nitrogen fixation processes.

Therefore, while it may be impolitic to disclose actually attained minimum costs it may be possible to establish particular facts and comparisons which will by their logic carry conviction as to the order of compared processes so far as production costs are concerned, without, however, expressing the exact differences in costs. For instance, by the "arc" process the factory cost of nitrogen in commercial nitric acid, excluding all power costs (derived by applying actual working records to a particular manufacturing site where all conditions are of the most favourable nature) is greater than the total cost of nitrogen in "cyanamid" including power at 10 dols. per continuous horse-power per annum (at a site where raw materials and labour are relatively high). Furthermore, taking that particular "arc" process which is the lowest in power consumption, the power cost alone, at eight to ten dollars per continuous horse-power per annum in weak nitric acid is greater than the total cost of "cyanamid," including power at the same cost per horse-power per annum (and at a site where raw materials and labour are high). These are actual comparisons and lead conclusively to some irrefutable deductions; first, that the "cyanamid" process can fix nitrogen cheaper than the cheapest of the "arc" processes, even although a charge of 10 dols. per continuous horse-power per annum is made against "cyanamid" and the power is given free to the "arc" process; second, if the cheapest of the "arc" processes, so far as power consumption is concerned, is charged only with power at the rate of 8 to 10 dols. per continuous horse-power per annum and the process is presented without cost or charge of any sort with all labour, raw materials, and supplies, its unit of nitrogen would cost more than the total cost of the unit of nitrogen by the "cyanamid" process. It also follows from these conditions that the total cost of the unit of nitrogen in commercial nitric acid made

by the "arc" process cannot by any chance be less than double the total cost of the unit of nitrogen in cyanamid made by the "cyanamid" process. We have seen that the really great application of nitrogen is at the ammonia end, and these comparisons are impressive in showing not only that there is no hope of the "arc" process working into ammonia production, but also, and what is of more importance, that the "cyanamid" process has to its credit a wide margin of saving in cost to span the gulf between "cyanamid" and nitric acid.

(To be continued).

WELSH NOTES.

(By Our Special Correspondent).

THE trade of Swansea Port during the past week was on the whole favourable, and only a fraction below the high-tonnage mark of the previous week, whilst, compared with the corresponding period last year, a large increase is registered. Imports improved considerably on the comparative slackness of the past few weeks, and patent fuel shipments were especially active. Chief among the imports were 980 tons iron ore from France, 1224 tons iron pyrites from Portugal, 1300 tons calamine from Algeria, and 6200 tons iron ore from Newfoundland. Shipments of tinplates amounted to 71,531 boxes, 86,058 boxes being received from works. Stocks in Dock warehouses stood at 241,377 boxes, compared with 226,850 boxes the preceding week and 219,230 boxes in the corresponding week of last year.

Trade at the Port Talbot Dock was brisk, the total tonnage being well up to the average. Among the imports were 2675 tons steel billets and pig-iron. Tinplates showed a slight improvement, whilst the steel works, copper works, and fuel works were busy.

All the industries of the Swansea Valley were again in full swing during the week, with the inevitable exception of the tinplate industry, where numerous stoppages were made for repairs and alterations. In one or two of the sheet mills, however, a shortage of labour was experienced, a handicap which has extended its influence to all departments of industry in the valley during the week. The Landore blast furnaces showed a large production of pig-iron, whilst every department of the Steelworks was exceptionally brisk. The copper trade remained good, but sulphuric acid factories experienced a very bad time again, and supplies of vitriol met with little sale. Chemical manure works seemed to be running as usual. There were no changes in the spelter industry, works being fully employed. Large supplies of lead-piping and safety-fuse offered met with a ready demand. Trade was brisk at the Mond Nickel Works and the Mannesman Tube Works, and supplies of material were not large enough to meet the demand. The Metal Extraction Works were well engaged, and iron and brass foundries were busy.

The steel and iron trade of the Dowlais Works was exceedingly brisk, the blast furnaces working for the seven days, mill and other finishing plant for six days, and the steel-producing plant for five days. The blast furnaces supplied the rough, molten metal for the steel producers and passed on a quantity of pig-iron to stock and for orders. The Bessemer and Siemens furnaces were employed in the manufacture of crude steel of various kinds. The Goat Mill produced large steel rails of heavy weight, steel ingots, sleepers, bars, and blocks of steel for shell cases. In the Big Mill fish-plates and sole-plates and tram-rails for colliery purposes were turned out.

The extended prohibition of exportation ofterne-plates, including tin boxes and tin canisters for food packing to Denmark, the Netherlands, Sweden, and Norway, is destined to cripple the already languishing tinplate industry in South Wales. To all these countries, however, with the exception of Norway, tinplates have been a forbidden

export for some considerable time, but licences had to some extent been granted on assurance being given that any plates covered by such licences would not be allowed to benefit enemy countries. It is understood that the reason Norway was not included before in the list of prohibited countries was due to an assurance from the Norwegian Government that no plates used should benefit enemy countries. Norway prior to the outbreak of war was making increasing use of tinplates for its fish-packing industry, which had been rapidly growing. This is plainly indicated by the fact that for the first five months of this year the number of boxes exported to Norway totalled 21,625 as compared with only 11,076 in the corresponding five months of last year.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 3, 1915.

Dr. ALEXANDER SCOTT, M.A., F.R.S., President,
in the Chair.

THE PRESIDENT announced the loss sustained by the Society through death of Dr. Hugo Müller and Sir Arthur H. Church. The President referred particularly to the distinguished part which these Fellows had taken in the furtherance of chemical science, and to the valuable services which they had rendered to the Society.

Dr. Hugo Müller was a member of the Council from 1863 to 1866, Foreign Secretary from 1869 to 1885, and was elected President in 1885. He continued to be an active worker until the end, his latest communication to the Society being received exactly a month ago.

Sir A. H. Church had twice served on the Council—from 1876 to 1880 and from 1887 to 1890.

Mr. A. L. Bacharach was formally admitted a Fellow of the Chemical Society.

Certificates were read for the first time in favour of Messrs. John William Lee, Belmont, Hasland, Chesterfield; Oswald James Walter Napier, B.A., public analyst, Dunedin, New Zealand; Archibald Ramsden Pearson, B.Sc., 491, Fulham Road, S.W.; Kodlapur Bhima Rau, B.A., Department of Agriculture in Mysore, Sankarapuram, Bangalore, India; Nugehalli Sampataiengar, Department of Agriculture, Mysore State, Bangalore, India; John Sewell, 166, Victoria Street, W.

The following papers were read:—

"A Thermal Study of the Carbonisation Process." By HAROLD HOLLINGS and JOHN WILLIAM COBB.

"The Properties of Cold-worked Metals." Part I. The Density of Metallic Filings. By THOMAS MARTIN LOWRY and REGINALD GEORGE PARKER.

"Syntheses of Benzo- γ -Pyrones and Flavones." Part IV. By SERGE JACOBSON and BROJENDRA NATH GHOSH.

"The Relation between the Infra-red and Ultra-violet Absorption and the Variation in Absorption with Concentration." By EDWARD CHARLES CYRIL BALY and FREDERICK GERALD TRYHORN.

"Ionic Dissociation and the Law of Mass Action." By EDWARD CHARLES CYRIL BALY.

June 17, 1915.

THE PRESIDENT referred to the loss sustained by the Society through death of Messrs. Francis Henry Neville; Thomas Law Patterson; Benjamin Ashwell Posford. (Killed in action).

The PRESIDENT also announced that at more than one of their meetings the Council had carefully considered the

question of removing from our lists the names of honorary and foreign members and of ordinary Fellows who are at the present time alien enemies of his Majesty King George. Whilst regarding with the deepest detestation and abhorrence the ruthless and barbarous methods adopted by the Germanic Allies, and more especially the debasement of chemical science by them as revealed in their latest operations, the Council had to-day by a large majority decided that no steps can, consistently with the dignity of the Society and with due regard to British ideas of justice, be taken in the above direction until after the cessation of hostilities.

Certificates were read for the first time in favour of Messrs. Ernest James Hoy, 39, Victoria Road, Higher Tranmere, Birkenhead; George Stanley Irving, 36, Red Rock Street, West Derby Road, Liverpool; Wilfrid Gustav Polack, M.Sc., Beacon Mount, Highlands Road, Runcorn; Vincent Harold Smith, Rudgewood Grange, Kingswinford, Dudley.

The following Certificates have been authorised by the Council for presentation to ballot under By-law I. (3):—Joseph Charles Kernot, 6, Via San Carlo, Naples, Italy; Arnaldo Piutti, 106, Rettifilo, Naples, Italy.

Messrs. R. W. Tonkin and A. J. Hale were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared as duly elected:—Frederick Louis Armitage; William Alfred Bromwich; Pinzen Cheng, B.Sc.; George Roger Clemo, B.Sc.; David Owen Davies; Albert Richard Henschley, M.D., L.R.C.P., L.R.C.S.; Frank Jagger; Frank Peachey, B.Sc.; Walter Ratledge Twigg.

The following papers were read:—

"The Rotatory Dispersive Power of Organic Compounds." Part IX. Tartaric Acid and the Tartrates. By THOMAS MARTIN LOWRY and PERCY CORLETT AUSTIN.

"A Study in the Coumarin Condensation." By BIMAN BIHARI DEY.

"The Formation of Heterocyclic Compounds from Hydroxymethylene Ketones and Cyanoacetamide." Part I. By HEMENDRA KUMAR SEN GUPTA.

"Nitrocamphor and its Derivatives." Part VIII. The Action of Formamide on Nitrocamphor. By THOMAS MARTIN LOWRY and VICTOR STEELE.

"Reactivity of the Halogens in Organic Compounds." Part VIII. Interaction of Alkalis and Alkali Bromoacetates and Bromopropionates in Methyl Alcohol Solution and in Mixtures of Methyl Alcohol and Water. By GEORGE SENTER and HENRY WOOD.

NOTICES OF BOOKS.

The Poison War. By ALFRED A. ROBERTS. London: William Heinemann. 1915.

This book appears at a very opportune moment, and is full of interest for the reader of the present day, while it will no doubt be of considerable historical interest in the future. It is to be hoped that it will be widely read, and that the definite and precise information it gives will be impressed upon the minds of the public, and will serve to correct the vague general ideas with which it would appear our national characteristics make us ready to remain content. A description is given in it of the three poisonous gases—chlorine, carbon monoxide, and nitrogen peroxide—which have been employed by the Germans. Some account is given of their chemical properties and of the tortures suffered by the victims of them. The apparatus employed for disseminating them is also described. The author further explains how the Germans are systematically poisoning the forces of the Allies at long range by means of white phosphorus in their artillery projectiles and rifle cartridges, a fact which has hitherto been unknown to the

public. The nature of different explosives, and the structure of shells, incendiary and other bombs, &c., are discussed, and the appendices contain translations of extracts from the Hague Convention. The author drew attention months ago to the probable usage of asphyxiating projectiles by the enemy, basing his conclusions upon observations made in the Balkans during the late war. He has brought together his data from all reliable sources, sifting it with the utmost care, and is indebted to French experts for much of his information.

The Magic of Experience. By H. STANLEY REDGROVE. B.Sc. (Lond.), F.C.S. London and Toronto: J. M. Dent and Sons, Ltd. 1915.

This book is intended for the general reader who is interested in philosophy, and will provide him with material for reflection and give him some insight into the views of Berkeley, Swedenborg, and others. The technical terms of philosophy are avoided as far as possible, and the book can be read without undue difficulty by the average well-instructed reader. The introduction is contributed by Sir W. F. Barrett, F.R.S., to whom the author is also indebted for many suggestions.

CORRESPONDENCE.

ORGANISATION OF CHEMICAL SCIENCE.

To the Editor of the Chemical News.

SIR,—In view of the great interest you have shown in the organisation of chemical science in this country, I enclose herewith copy of a letter which the Council have sent to the Fellows of the Chemical Society.

The necessity for the co-ordination and organisation of the various branches of chemical science and their application is of the utmost importance to the Empire, and this fact is gradually becoming evident to the general public. There is, however, urgent need for the nation to realise still more fully the cardinal importance of this subject, and in view of the great powers wielded by the press to create and mould public opinion, I venture to hope that you will not only find space for the letter in your columns, but that you will direct the attention of your readers to it, and to the national importance of the efforts of the Chemical Society to grapple with this problem.—I am, &c.,

ALEXANDER SCOTT, President.

Chemical Society, Burlington House,
London, W., July 2, 1915.

THE CHEMICAL SOCIETY.

DEAR SIR,—In March last the Council of the Chemical Society presented to the Prime Minister a memorial on "The Position of the Chemical Industries" in this country, and asked him to receive a deputation from the Society to explain in greater detail the opinions set forth therein. A similar memorial had also been presented by the Royal Society, and on May 6 the Presidents of the Boards of Trade and Education received a joint deputation from the two Societies. The deputation assured His Majesty's Ministers of the loyal desire of the Fellows of both Societies to assist the Government, and promised their hearty co-operation in all that could be done to utilise the great but latent chemical talent of the nation.

As the war proceeds, the paramount part which chemical science is playing and is destined to play in the present struggle becomes daily more evident to everyone, and in pursuance of the assurance given to the President of the Board of Trade, the Council has constituted itself a Consultative Body, which will meet at frequent intervals to consider, organise, and utilise all suggestions and inventions which may be communicated to it, and will report on the same to the proper authorities. In this work it will have the assistance of Committees specially qualified to deal with individual problems, the nature of which will

doubtless be very diverse. The Council is of opinion that much can be done in this way to relieve the overwrought Government departments of work which would probably appear less complex to such Committees of chemical experts.

This Consultative Body having now been formed, the President and Council invite the Fellows of their own and kindred Societies to forward, *in strict confidence*, suggestions and inventions for its careful consideration. However trivial some of these suggestions may appear if taken alone, it is always possible that when brought into correlation with others they may lead to results of great value, and it is this process of correlation and subsequent presentation to the suitable Government authorities which the Council has in view.

All suggestions should be addressed to "The Council of the Chemical Society, Burlington House, London, W.," and will be regarded as confidential by the Council, which feels that it may rely on the loyal and energetic co-operation of the Fellows in this attempt to render assistance to the Empire.

It is of great importance that the Council should know on whom it can rely for help, and the nature of the services each Fellow can render; it will be of considerable assistance, therefore, if you will kindly fill in and return the form attached.

(Issued by the authority of the Council),

ALEXANDER SCOTT, President.

July 1, 1915.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clx. No. 20, May 17, 1915.

Tri-magnesium Citrate and the Supposed Basic Citrates of Magnesium.—E. Léger. —When tri-magnesium citrate is prepared by saturating a concentrated hot solution of citric acid with magnesium carbonate, the salt containing $13\text{H}_2\text{O}$ crystallises out very slowly. This is due to the formation of a salt containing less than thirteen molecules of water, which is slowly hydrated; it is much more soluble in water than the salt containing $13\text{H}_2\text{O}$. When a concentrated solution of tri-magnesium citrate is heated on the water-bath for twenty hours the liquid becomes turbid, and a crystalline precipitate, insoluble even in boiling water, is deposited. This is a hydrate containing $9\text{H}_2\text{O}$. By mixing two boiling alcoholic solutions of acetate of magnesium and citric acid a citrate containing 7 to 8 H_2O is obtained. The author has repeated Kämmerer's work on the basic magnesium citrates, but has not succeeded in obtaining the compounds described by him.

Synthesis of α -Glycerophosphoric Acid.—O. Bailly. —Calcium α -glycerophosphate can be prepared as follows:—A solution of potassium permanganate is added to a solution of sodium allyl phosphate, and the MnO_2 formed is filtered off. Then a solution of calcium chloride is added, the slight precipitate of $\text{Ca}_3(\text{PO}_4)_2$ is separated, and alcohol is added. A precipitate of α -glycerophosphate of calcium is thus obtained.

Liebig's Extract of Meat Company, Limited.—At the Board Meeting, on June 28, it was resolved that, subject to confirmation at the fiftieth ordinary general meeting of the company, to be held on July 21, an additional dividend of 10 per cent and a bonus of 2s. 6d. per share, both free of income-tax, on the ordinary shares for the year ended March 31, 1915, shall be payable on and after July 22 to proprietors who are registered on the company's books on July 12, and to holders of ordinary share warrants to bearer. This dividend and bonus, together with the interim dividend paid on February 15 last, amounts to 22½ per cent free of income-tax for the year.

THE CHEMICAL NEWS.

VOL. CXII., No. 2903.

THE

MOLECULAR WEIGHT OF SODIUM SULPHATE AND THE ATOMIC WEIGHT OF SULPHUR.

By THEODORE W. RICHARDS and CHARLES R. HOOVER.

THE preparation and neutralisation of pure sodium carbonate, for which the way had been cleared by the work described in a foregoing paper (CHEMICAL NEWS, cxii., 5 *et seq.*), provides a standard of reference for many other precise determinations. The present paper discusses briefly a series of determinations of the ratio between sodium carbonate thus prepared and sodium sulphate made from it by exact neutralisation with sulphuric acid. This comparison had already been attempted long ago by one of the authors (*Proc. Am. Acad.*, 1891, xxvi., 268; *Zeit. Anorg. Chem.*, 1892, i., 180). The old determinations were, however, made only as a side issue in the course of an extensive study of the atomic weight of copper; they showed a rather large range of error, and were made with sodium carbonate which was then known to contain traces of silica (*Ibid.*, 247 and 157 respectively). Moreover, our recent work on the fusion of sodium carbonate showed that this older specimen, merely dried at a dull red heat, must have contained traces of water also; therefore it seemed well worth while to repeat the experiments with modern precision.

The programme here was simpler than that involved in the immediately preceding research on carbon. The fused sodium carbonate was carefully weighed, and treated in the platinum retort with a very slight excess of pure sulphuric acid; the solution was then freed from carbon dioxide and evaporated quantitatively in a quartz flask without boiling, but with the help of a current of air, and the remaining salt was fused and weighed.

Preparation of Materials.

Most of the materials were prepared just as before, the same three samples of sodium carbonate being employed. The sulphuric acid was made from the purest acid of commerce (which contained only minute traces of impurity) by three successive distillations in a non-tubulated glass retort over a ring burner. Only the middle portions of each distillate were used. Among other substances sought in this acid was selenium, which was tested for in a 20 cc. portion of the original substance by dilution with twice its volume of water, treatment with half its volume of concentrated hydrochloric acid after cooling, and then boiling until the mixture occupied about 35 cc. No free chlorine was detected during this process, and the solution upon treatment with sulphur dioxide showed no red coloration. This test is supposed to show 0.003 per cent of selenium; therefore presumably this element was absent. The quantitative outcome, to be given later, certainly indicates that no element with a greater atomic weight than sulphur was present, confirming the qualitative test. The pure redistilled acid was diluted with pure water to a convenient standard concentration, suited to the capacity of the weighing burette and the amount of carbonate to be neutralised.

The preliminary standardisation of the standard solution of acid was carried out as follows, much more simply than in the final experiments. This simple preliminary procedure is within the scope of the apparatus in any laboratory, and may be useful to those wishing to

standardise an acid solution. A quantity of air-dehydrated, thrice recrystallised sodium carbonate was placed in a weighed platinum crucible. This was heated on a pipe-stem triangle while dry carbon dioxide was passed in through a Rose crucible lid, the usual porcelain delivery tube having been replaced by a slightly longer hard-glass tube. After having been kept at a temperature below fusion for some time the salt was carefully fused and kept in a liquid condition for a few minutes. It was then cooled in a current of carbon dioxide and weighed again. The crucible and contents were placed in a weighed quantity of the standard solution of sulphuric acid known to be insufficient to neutralise all the carbonate, and the liquid was heated nearly to boiling after the addition of the mixed indicator. When the acid had been exhausted the effervescence naturally ceased, and the solution of the carbonate proceeded very slowly; therefore it could be easily determined when more acid was needed. Adding acid drop by drop from time to time, the carbonate was finally dissolved and the solution remained neutral. The process may, of course, be conducted with even less trouble by adding at first a slight excess of acid and titrating back with hydroxide. By this crude method 1 grm. of sodium carbonate was found to be equivalent to 41.032 grms. of acid solution, while in the more carefully executed titration in the first regular analysis, 1 grm. of pure sodium carbonate was found to be equivalent to 41.0280, or a difference of 1 part in 10,000. This is a degree of accuracy far exceeding that possible by the ordinary methods used for the volumetric neutralisation of sodium carbonate, which gives rather questionable results in inexperienced hands. (The uncertainty due to the indicator alone may amount to as much as 0.5 per cent. in the presence of carbonic acid.—See A. A. Noyes, *Journ. Am. Chem. Soc.*, 1910, xxxii., 815). The standard acid evidently contained 2.255 per cent of H_2SO_4 .

An auxiliary solution, 100 times less concentrated, was next prepared by diluting a weighed amount of the main standard solution with a weighed amount of water. These solutions were kept in resistant glass bottles with paraffin-covered rubber stoppers and paraffin-coated syphon tubes. Air was admitted through large U-tubes filled with beads, and with portions of solution removed from time to time from the bottles. That a dilute solution may be preserved without appreciable change in concentration was shown by the results of the titration of hydrobromic acid against sodium carbonate, described in the previous paper.

The Neutralisation and Determination.

The exact titration of accurately weighed amounts of the purest fused carbonate against sulphuric acid was carried out essentially as in the case of the hydrobromic acid. The end-point chosen was slightly more on the acid side of exact neutrality, the hydrogen ion concentration being about 10-6, because the excess of acid could be driven off during the subsequent ignition. The non-volatility of sulphuric acid from aqueous solution allowed more variation in the method of reaching the end-point than in the earlier case. The quantity of the main sulphuric acid solution required to combine with the observed weight of sodium carbonate was weighed out, and the carbonate was dissolved in the acid in the platinum retort. In determinations 2, 3, and 6 the neutral point was reached by several further very small additions of very dilute acid, as in the earlier case. In Nos. 4 and 5 a slight excess of sulphuric acid was added in the first operation, and the solution was titrated back with standard sodium hydroxide solution from a weighing burette. In No. 1 a very slight excess of acid added was removed by repeated evaporation and ignition of the sodium sulphate to constant weight, followed by thorough fusion in a rapid current of air. These different methods of treatment, by substantially agreeing as to their results, established the fact that the carbon dioxide had been completely expelled from the solution when the end-point was

* Contribution from the Wolcott Gibbs Memorial Laboratory of Harvard College. From the *Journal of the American Chemical Society*, xxxvii., No. 1.

reached in the hydrobromic acid analysis described in the preceding paper.

After the solution of sodium sulphate had been rendered neutral or slightly acid, it was concentrated by passing pure air over the solution in the covered platinum retort until the volume indicated that the solution would be slightly more than saturated at room temperature. It was then transferred while warm to a small quartz flask, in which it was to be evaporated and fused somewhat in the manner employed in a previous research upon silver nitrate (Richards and Forbes, Carnegie Inst., Wash., 1907, Pub. lxi., 51; *Journ. Am. Chem. Soc.*, 1907, xxix., 808). In the present case, however, the flask had the tube for admitting the air fused into the top of the flask, and a side exit tube attached, after the fashion of a gas washing bottle. Both tubes were provided with ground quartz stoppers. The flask had a capacity of about 100 cc. and was not too large to weigh accurately. The transference from the retort to this flask was naturally the most delicate part of the work. By placing a curved glass rod within the retort with the curve emerging tangent to the inner edge, but free from the outside portion of the rim, it was possible to pour the solution from the retort along the rod without danger of loss. A small funnel tube, drawn out and bent slightly at its extremity, guided the stream well down into the inlet tube of the quartz flask, and the transfer was facilitated by clamping the flask in an inclined position. The flask having been filled to within a short distance below the end of the inlet tube, was placed in an electric heater, maintained at a temperature just insufficient to cause ebullition, pure air being passed in through a glass tube ground to fit the quartz inlet tube. The retort cover and condenser were then thoroughly rinsed, and the solution with several wash waters placed in the platinum retort and concentrated to small bulk; then the solution was added to the contents of the quartz flask. Generally, three such series of washings were carried out until it was certain that every weighable trace of salt had been transferred. After the sodium sulphate solution had been completely collected in the quartz flask and dried, the large electric oven, which had completely enclosed the flask, was exchanged for another, consisting of a fire-clay tube wound for a higher temperature, and large enough to enclose only the bulb. With this heater a temperature just sufficient to fuse the edges of the mass of sulphate was maintained for several hours, after which the temperature was raised for a short time to the point necessary to fuse the salt (about 875°). A current of pure air was passed through the flask throughout all these steps. It was found that two hours' heating at the lower temperature (about 850°) produced constant weight, and that on fusion only a very small apparent loss in weight appeared, the average in five trial determinations being 0.01 mgrm. per gm. of salt. This absence of a decrease in weight shows that very little water was retained within the porous, brittle solid at this high temperature. The final calculation was, of course, made on the basis of the weight of salt after fusion, and for the purpose of correcting this weight to the vacuum standard the density of fused sodium sulphate (previously unknown) was determined as follows:—6.07615 and 8.43725 grms. of salt (in *vacuo*) displaced 1.9519 and 2.7063 grms. (in *vacuo*) of toluene respectively, the toluene having a density of 0.8661 at 20°. The two determinations yielded as results 2.696 and 2.700 for the density respectively, or in the mean 2.698.

The weighing of vessels of quartz or glass as large as the flasks and burettes used in this work is accompanied always by some difficulty, but if the vessels are provided with precisely similar counterpoises, and if each piece of apparatus is kept in a separate desiccator and each weighed under precisely the same conditions after the same time, good results may be obtained. In this work of course the weights were carefully standardised, the counterpoises were made of volume and weight like those of the objects to be weighed, the weighing room was carefully guarded

as to constancy of temperature, corrections for changes of pressure were applied when needed, and the customary details necessary for accuracy were faithfully heeded. The keeping of the small tube of radio-active material in the balance case greatly helps in the discharge of electrical charges, always so troublesome with large non-conducting vessels. The ideal laboratory conditions possible in the new laboratory, built especially for this kind of work, greatly facilitated the convenience of the task and accuracy of the outcome. The results of the comparison of sodium carbonate with sodium sulphate are given in Table I. In the first column is given the number of the experiment, in the second the sample of sodium carbonate, in the third the weight of sodium carbonate *in vacuo*, in the fourth the weight of sodium sulphate, in the fifth the weight of this latter salt corresponding to 1 gm. of sodium carbonate, and in the last column the atomic weight of sulphur—assuming that the molecular weight of sodium carbonate is 105.995, sodium being 22.995, and carbon 12.005, as found in the preceding investigation. The maximum deviation from the mean is less than 0.003 per cent of the molecular weight of the sodium sulphate, and the "probable error" of the average value is less than 0.001.

TABLE I.—The Ratio between Sodium Carbonate and Sodium Sulphate.

No. of expt.	Sample of Na ₂ CO ₃ .	Weight fused Na ₂ CO ₃ (in vac.). Grms.	Weight fused Na ₂ SO ₄ (in vac.). Grms.	Weight of Na ₂ SO ₄ from 1.00000 grms. Na ₂ CO ₃ .	Atomic weight sulphur.
1	A	5.25191	7.03820	1.34014	32.058
2	B	4.50977	6.04382	1.34016	32.060
3	B	5.04233	6.75737	1.34013	32.057
4	B	3.67340	4.92304	1.34019	32.063
5	C	4.18724	5.61151	1.34015	32.059
6	C	4.55100	6.09916	1.34018	32.062
Sum ..	..	27.21565	36.47319	Av. 1.340155	32.060

Thus it is clear that 1.00000 part of sodium carbonate is equivalent to 1.340155 parts of sulphate; hence, if silver is taken as 107.88 and sodium carbonate as 105.995, NaSO₄=142.050 and sulphur is found to 32.060. This figure is only a little below the value 32.069 found at Harvard eight years ago by a more direct method—the conversion of silver sulphate into the chloride (Richards and Grinnell Jones, Carnegie Inst., Wash., 1907, Pub. lxi., 69; *Journ. Am. Chem. Soc.*, 1907, xxviii., 826). The substantial agreement of the results affords good evidence that the roundabout comparison adopted in the present research is trustworthy in each of its varied steps, and incidentally confirms the value for carbon given by the foregoing research. Evidently we cannot be far wrong in assuming that the correct value for the atomic weight of sulphur is the mean between the two results—that is to say, 32.065. If silver is taken as 107.871 (instead of 107.88) this value becomes 32.056.

The comparison of the ratio of sodium carbonate to sodium sulphate with the old results of 1891 is not without interest. The average of all the old results (*loc. cit.*) made the ratio 1.0000:1.3399, while the average of the last three most trustworthy results made it 1.0000:1.3400 (instead of the new value, 1.340155). The respective errors of the older averages were thus 0.0022 and 0.011 per cent. Errors of this sort are precisely of the order caused by the retention of water in the unfused sodium carbonate employed in the early work, and there can be little question that this substance must have really contained in 1891 at least as much water as we found it to contain in 1913 under similar circumstances (see preceding article). The sodium sulphate had been fused then as now; hence the atomic weight of copper as found in 1891 by comparison with sodium carbonate must have been lower than the truth by perhaps 0.022. Correcting, we find the recalculated atomic weight of copper

to be 63.554 (instead of 63.532), a value much more nearly agreeing with that found from the direct comparison with silver, namely, 63.57. (This recalculation is of the figures on the top of p. 271, *Proc. Am. Acad.*, 1891, xxvi. Na_2CO_3 is assumed as 105.995 above instead of as 106.108, as it was twenty years ago).

This investigation, like the foregoing, was conducted under the favouring auspices of the Carnegie Institution of Washington.

Summary.

The quantitative conversion of pure fused sodium carbonate into pure sodium sulphate is described, the ratio of the equivalent weights of these substances being found to be 1.00000 : 1.340155. Assuming $\text{Na}_2\text{CO}_3 = 105.995$, as found in the preceding research ($A_g = 107.880$), the molecular weight of sodium sulphate becomes 142.050 and the atomic weight of sulphur becomes 32.060. This is in reasonable agreement with the earlier Harvard value, 32.069, and the mean of the two, 32.065, may perhaps be taken with some confidence as the most trustworthy value thus far recorded. This research, like that immediately preceding it, has been useful in confirming by cross-reference many varied methods and results and in eliminating slight apparent inconsistencies in earlier results, and the outcome seems to strengthen our confidence in the processes upon which our present table of atomic weights is founded.

THE CYANIDE PROCESS.*

By FRANK S. WASHBURN.

(Concluded from p. 22).

THE first step in the derivation of nitric acid from cyanamid is to convert the latter into dry ammonia gas. Such conversion is now conducted in so many places and on so large a scale that the actual cost of the operation, including all losses, is no longer a matter of speculation or approximation. The efficiency has been raised in actual practice to over 99 per cent, and the cost, while not negligible, is so low as to add only a small percentage to the ordinary cost of the unit of nitrogen in "cyanamid." Therefore, the facts just set forth as to the cost of the unit of nitrogen in "arc" process nitric acid, compared with the cost of the unit of nitrogen in cyanamid, apply as well to the cost of the unit of nitrogen in pure ammonia gas. Roughly speaking, therefore, there is to the credit of the ammonia, available for oxidising it to weak nitric acid, fully one-half the cost of weak nitric acid derived by the "arc" process. As a matter of fact, the indications are that this span will be bridged by the absorption of not more than one-half this difference, making weak nitric acid by the "cyanamid" process cost approximately three-quarters of the "arc" process. As power is brought below 10 dols. per continuous horse-power per annum, production costs by the "arc" processes approach more nearly to costs by the "cyanamid" process. It is possible to make the general statement that the costs per unit of nitrogen in weak nitric acid may be taken as the same for both processes where power costs about 4 dols. per continuous horse-power year.

Comparison of the costs of ammonia gas by the "cyanamid" process and the "Haber" process show, broadly speaking, that the Haber process in its most favourable environment involves a cost nearly double that of the "cyanamid" process under favourable conditions practicable of attainment.

It must not be understood that the "cyanamid" process has exhausted the possibilities of further economies in manufacture. As examples, in one new factory study in which the requisite coke is to be made by local by-product ovens, the operations so balance that the fuel gas derived

is the quantity required, and as the tar and ammonia products pay for the coking, the coke is had at the price of coal. Where ammonia is derived at the cyanamid factory the sludge from the autoclaves composed of calcium carbonate and carbon may be turned back through the carbide furnaces and maintained in the cycle practically indefinitely as a carrier of nitrogen.

However, the whole story is not involved in a study of production costs, for there are other factors which may have a deciding voice, and of these we may mention as important the amount of the necessary investment for a given output, the salvage in the case of ultimate abandonment, the ratio of interest charge to the out-of-pocket expense, bearing in mind that the latter may be very much reduced by improved operating means while the former is fixed for all time. Taking the necessary investment in the "arc" process per unit of nitrogen in weak nitric acid as a basis, and assuming power to be placed upon the switchboard at an investment cost of 50 dols. to 75 dols. per horse power, the corresponding investment in the "cyanamid" process for a unit of nitrogen in weak nitric acid would be about one-half, and as cyanamid or ammonia gas about one-third. It is believed that the Haber process in the United States on the same basis would involve an investment of about two-thirds to three-fourths of the "arc" process. In the contemplation of any enterprise requiring large fixed capital there is a reasonable amount of capital beyond which objections to an increased amount are not to be measured by applying the interest and amortisation rate to the estimated costs of production. Converting a vast amount of gold in the bank into bricks and mortar, special machinery and appurtenances, particularly in the application of a new and special art, is a serious risk for which there is no exact measure, but which in contemplating the risk should weigh heavily as a guide to judgment.

In the case of ammonia production by the "cyanamid" process the fixed investment may be as low as one and one-half times the annual value of the product and in the case of the Haber process three times. In the case of nitric acid by the "cyanamid" process the investment may be as low as one and one-fourth times the annual value of the product, and in the case of the "arc" process with a power investment of 75 dols. per continuous horse-power the fixed investment would be between three and four times the market value of the annual product.

The majority of manufacturing concerns in the United States vary in fixed investment from one to one and one-half times the value of the annual product, and the inherent risk in industrial enterprises for reasonably assured profits demand, for the most part, very special conditions where this proportion is exceeded. Even that class of investments considered most stable as to reliability, permanency, and growth, namely, public utility corporations, do not exceed 4 dols. to 6 dols. investment per dollar gross revenue. We are therefore met in the case of the Haber and arc processes with the necessity for making an investment which, in the judgment and practice of the industrial world, is wholly out of proportion to the market value of the annual product, while in the case of cyanamid the requirements are within the limits of ordinary commercial practice.

These considerations serve to emphasise the difficulties in commercially advancing any new enterprise. The younger technical men do not encounter these difficulties and therefore do not give them due weight. There is extraordinary difficulty, particularly in the United States, in financing a new chemical enterprise, particularly if it involves a large preliminary expenditure in research and developmental work. The banker's attitude, and properly so, is to compare assets and liabilities. Buildings, equipment, and manufacturing sites are acceptable assets notwithstanding that in many companies if the business itself were abandoned there would be little or no value in the physical properties. Knowledge, processes, and ideas are not impressive assets. They are considered in large part

* From the *Chemical Engineer*, xxi., No. 5.

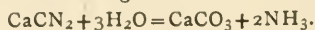
to have been something secured at great cost, but, even with good patent protection, practically available for the use of prospective competitors without cost to them. In some other countries such enterprises are viewed quite differently, notably in Germany, where ideas are the foundation of great and profitable enterprises and where by law and practice they are better protected for the exclusive use of those who have developed them than in this country.

The promise, or even the assurance of reasonable profit, is seldom a sufficient inducement to the investor to undertake a pioneer enterprise. The competitive element which dominates almost every other activity is lost sight of by the amateur promoter. He forgets that to the mind of the prospective investor he is in the sharpest kind of competition with those presenting other types and kinds of enterprises demanding capital. His project must grip the imagination with peculiar attractiveness as well as impress the practical sense of those to whom it is brought as not only being prospectively profitable but also assuredly safe with a minimum prospect of loss and a maximum prospect of profit. Of the many subordinate advantages there may be specifically mentioned an early dividend-paying period, a ready market for the securities, their acceptance as good collateral, and a ground-floor prospect in future extensions. In the end it must outweigh, in some cases, literally scores of other projects all claiming equal if not superior merit in every particular. There is another consideration of kindred merit which will be impressive if one considers that in a thing so extensively engaged in as trade in securities, one of the very largest activities in which mankind interests itself, there must grow up inevitably certain more or less arbitrary rules, practices, and points of view. These all turn naturally upon the usual thing, and the usual thing is the established industry, or at least an enterprise engaged in an established industry. Therefore, the new thing has a slow and difficult road to travel and its difficulties are more than in direct proportion to the amount of capital demanded. Those fixation processes which employ and own their own water powers make a plea to capital that others cannot make, for the reason that it can generally be shown that, should unexpected competitive developments in the remote future drive the undertaking to an unreasonably low return upon the investment, the rental value of the water power for other purposes will probably insure the continuance of a satisfactory return upon the total investment.

Even if it were granted that the "cyanamid" process is prospectively to play the leading rôle in the fixation of atmospheric nitrogen so far as the most important use of nitrogen is concerned, namely, in agricultural fertilisers, and even if it were further granted that it is the logical source of nitric acid, the question may still be an important one as to whether the raw product of this process may be looked to as the source of a long and important line of nitrogen derivatives. The fact is that there is an almost interminable line of derivatives which can be produced from cyanamid with the greatest technical success and assurance, and their manufacture has proved to be in some cases commercially feasible. The direct and valuable application of the raw product, cyanamid, is unique in air nitrogen fixation processes. The proof of this value lies in the fact that fully 80 per cent of the entire annual product of normally 15,000,000 dols. value is sold as the raw product.

The principal derivative at the present time is ammonia, which has earlier herein been referred to. None is being made in America at this time outside of the Cyanamid Company's research laboratory, but abroad various plants are producing some fifteen tons of gas per day, part of which goes into high-grade sulphate for fertiliser use and part into anhydrous ammonia. There is also installed and about ready for operation a large Norwegian plant erected for the Birkeland and Eyde interests for transforming some sixty tons of cyanamid per day into ammonia, which will be absorbed in nitric acid for the production of

ammonium nitrate. The transformation takes place according to the following reaction—



This decomposition is accomplished by the use of water and high-pressure steam in autoclaves, and large-scale working plants show an efficiency of over 99 per cent nitrogen transformation. The ammonia gas is delivered from the autoclaves mixed with steam and absorbed directly in sulphuric acid without removal of the steam, or passed through a very small ammonia column equipped with condensers and coolers for the removal of the steam, thereby yielding a very high-grade pure ammonia gas. In case it is desired to make anhydrous ammonia it is simply necessary to intensify this drying action and compress the gas; considerable quantities of this ammonia are sold in France in the anhydrous state. The cost of the transformation is almost negligible, as the units have very large capacity and require very little attention.

Cyanamid in the presence of water tends to transform itself slowly to dicyandiamid, and this latter to urea. Methods have been recently evolved which make practicable these transformations either to urea or dicyandiamid with approximately 90 per cent efficiency and obtain chemically pure salts as the end product. Dicyandiamid, formula H_2CN_2 , contains 66.6 per cent nitrogen, or probably the highest concentration of any staple nitrogen compound. It has been proposed for use in explosives, acting as a deterrent, also for use in the dye industry. Its greatest future possibly lies in the ease with which acids transform it into the guanidines, which should find large uses in the explosive industry. The material has been proposed for use as a fertiliser because of its high nitrogen content, but it is probable that its slow decomposition in the soil will never warrant its use for this purpose.

The United States is importing about 50,000 dols. worth of high-grade urea annually for the celluloid industry alone, and could this material be cheaply produced there is no doubt but that it would find an even greater use in the explosive industry. Considerable quantities of this material have been produced in the research laboratory, which has been tried by the celluloid manufacturers with perfect success. It is now practicable to replace the importations of this expensive salt.

In the field of organic derivatives of cyanamid there is practically no end to the series that have developed abroad. The latest addition to this group has been creatin, which seems to be getting somewhere close to synthetic foods.

The calcium in the calcium cyanamid can be replaced by the heavy metals, and recent experimenting with some very interesting compounds, such as lead cyanamid and copper cyanamid, promise valuable results.

When certain grades of cyanamid are melted with common salt the free graphite in the original material is combined with the calcium cyanamid forming cyanide. A transformation of better than 90 per cent nitrogen efficiency is obtained and the resulting product contains approximately 25 per cent KCN equivalent. This material, which can be prepared so as to deliver it into the hands of the consumer at about two-thirds the present price of high-grade cyanides, requires solution in water and filtration. Both operations are easy, and the filtrate can be used in the place of cyanide for the extraction of precious metals. Large scale experiments have been tried out in various cyanide works throughout the world, and in every case it has proved to be identical in behaviour with regular cyanide, showing the same extraction efficiencies. The lower price at which this material can be delivered to the consumer more than takes care of the very simple extra dissolving and filtering operations incident to its use, and there should be, therefore, a very large field for this material supplanting the more expensive, high-grade cyanide.

Naturally when the transformation to cyanide is so

simple it is also possible to manufacture ferrocyanide, and enter into the case-hardening field and other uses for this material. As a matter of fact, cyanamid itself can be very simply compounded into a case hardener which is the equal of any of the present materials on the market, and superior to most of them. The German cyanamid makers have, since the beginning of the war, been swamped with orders for this case-hardening material, sold under the name of "Ferrodur."

Reference has been made heretofore in this paper in a general way to nitric acid production from ammonia. There has been developed recently a new process of re-oxidising ammonia to nitric acid at high efficiency. It is believed to do away with all of the limitations of the Ostwald process, and, if so, the industry will be in a position to meet nitric acid demands by way of cyanamid at a cost under conditions existing in the United States below anything any other process can offer. The gases leaving the oxidising chambers are many times more concentrated than those from the "arc" process furnaces, and, therefore, condensation is greatly simplified and recovery much increased. The units can be made large or small and their cost is rather low, so that small nitric acid plants can be installed at almost any place in the country within shipping range of the cyanamid plant, it being autoclaved into ammonia and converted into nitric acid at the point of use.

Quite recently the American Cyanamid Company has been using the "cyanamid" process as a means of producing argon gas in quantities, producing the nitrogen by means of the copper process and later eliminating the nitrogen by continued re-absorption in the cyanamid ovens, leaving argon as the final gas. Thousands of feet of this gas, highly concentrated, is being sold to the lamp industry, chiefly for American use, but in part to consumers abroad at the home of the chemical industry.

THE EXTENSION OF THE SPECTRUM BEYOND THE SCHUMANN REGION.

By THEODORE LYMAN,
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THE violet limit of the spectrum determined by direct eye observation lies in the neighbourhood of 4000 Angstrom units; with a glass prism and lenses the spectrum may be followed photographically to wave length 3000 or thereabout; with a quartz system or with a reflecting grating, the limit may be pushed to wave length 1850. Victor Schumann showed that the absorption of the air and of the gelatin of the photographic plate were responsible for the abrupt termination of the spectrum. By employing a vacuum spectroscope and a special photographic plate whose emulsion was very poor in gelatin, he was able to push his observations to wave length 1230. At this point he was stopped by the opacity of the fluorite of which his lenses were made.

I have employed a vacuum spectroscope containing a concave diffraction grating ("The Spectroscopy of the Extreme Ultra-Violet," Longmans, Green, & Co.) arranged in such a manner that the light path from the source to the photographic plate is wholly in gas. Briefly, the apparatus may be described as a brass tube about 11 cm. in diameter and rather over a metre long. This tube is closed at each end by brass plates ground to fit suitable flanges. In my most recent experiments the light is generated electrically in a discharge tube of quartz provided with tungsten electrodes. This discharge tube fits air-tight on one of the two brass plates just mentioned; light from it having passed through a slit, traverses the length of the apparatus and falls upon the diffraction grating by which, having been analysed into its component colours, it is brought to focus on a special photographic plate placed in close proximity to the slit.

As the discharge tube is in no way separated from the body of the spectroscope it is obviously necessary to choose for the experiment some gas which will not only yield radiations in the region under investigation but which will be transparent to these radiations. My earlier experiments were conducted with hydrogen, since it had shown the necessary characteristics in that part of the spectrum investigated by Schumann. With this gas at a pressure of 2 or 3 mm., and by employing a strong disruptive discharge, about eighteen months ago I was able to extend the spectrum to wave length 900.

A tedious investigation having convinced me that nothing more was to be expected from the use of hydrogen, at least in this neighbourhood, I turned my attention to helium, being guided by some of my earlier experiments which had proved that this gas possesses the necessary transparency. At the same time, I made some improvements in my apparatus which, though they left its general form unchanged, resulted in making it far more air-tight than ever before. The success of this improvement may be judged by the fact that I have recently been able to leave the spectroscope for over fourteen hours at a pressure of about 3 mm. without being able to detect any leak, either by a McLeod gauge reading to 0.007 mm. or by the appearance of impurities in the spectrum of the gas content. I also took particular pains to purify the helium which I employed.

I have been rewarded for my trouble by a very considerable extension of the spectrum, for with helium free from nitrogen, at a pressure of 2 or 3 mm., by the use of the disruptive discharge, and with an exposure of about ten minutes, I have repeatedly observed a number of new lines the most refrangible of which has a wave length of 600. All this has been accomplished with a grating ruled on speculum and with photographic plates prepared exactly as recommended by Schumann. The wave length 600 represents an extension beyond Schumann's limit greater than that which Schumann himself achieved beyond λ 1850.

The relations of the spectra of hydrogen and helium have recently come into prominence through the theoretical researches of Bohr, Nicholson, and others. It so happens that the region on the more refrangible side of wave length 1250 offers an important ground for the study of these relations. In order that the conclusions may be of value, however, it is necessary that the gases under observation should be free from impurities. In the best form of closed discharge tubes the difficulties arising from the contamination of the gas by the material of the tube or by the electrodes are very considerable, especially when a disruptive discharge is used. In my apparatus, where the brass spectroscope and quartz discharge tube communicate directly, these difficulties are considerably increased. I trust in time to overcome them; but for the present I must confine myself to the following statements.

Prominent in the spectrum of hydrogen is the line at 1216 which forms the first member of a series predicted, on theoretical grounds, by Ritz. I have also found the two next members near wave length 1026 and 972. With hydrogen they are best seen when a disruptive discharge is used, but with helium containing that trace of hydrogen so difficult to remove, they occur quite strongly with a simple alternating current from a 60 cycle transformer. This is a good illustration of the curious behaviour of helium, for an atmosphere of this gas seems sometimes to facilitate the production of the spectra of other gaseous substances which occur in it as impurities. As far as I am able to observe with the uncondensed discharge, all the lines seen with helium are also found in hydrogen. It is only with the disruptive discharge that the new lines on the more refrangible side of λ 900 make their appearance; they occur in helium alone and number seven or eight; some are quite strong.

The wave length of the X-rays as determined by the Braggs is of the order of one Angstrom unit. There is,

therefore, a gap of some six hundred units between the region of the ordinary Röntgen rays and the limit which I have reached. Several attempts have been made recently to produce less refrangible X-rays (J. J. Thomson, *Phil. Mag.*, London, 1914, xxviii., 620; E. R. Ladd, *Ann. Physik*, Leipzig, 1915, xlvii., 605), but there is no satisfactory way of estimating their wave length unless perhaps one relies on the Planck-Einstein formula $Ve = h\nu$. Taking V as the potential drop which gives the cathode particle the velocity necessary to produce a very soft X-ray, e as the charge on the particle, and giving h the usual value ascribed to Planck's constant, the experiments of Dember (*Berlin, Verh. D. Physik. Ges.*, 1913, xv., 560) were made to yield a wave length for the X-ray longer than that which I have determined. Such speculations, though they are very interesting, cannot be given any great weight. There is still a considerable region between wave length 600 and wave length one which must be experimentally explored.

My present limit is set by the adjustment and dimensions of my apparatus. Now that we know that a Schumann plate can be used and that a speculum grating is efficient, I see no insuperable difficulty to a still further extension by purely spectroscopic means.—*Proceedings of the National Academy of Sciences*, June, 1915, i., No. 6.

ZIRCONIA, A NEW REFRACTORY.

By H. CONRAD MEYER.

AMONG the numerous so-called rare elements zirconium has to within the last few years ranked as technically unimportant. The development of the electric furnace, requiring for its construction bodies having an extraordinarily high degree of refractoriness, has probably been an important factor in calling the attention of the electro-metallurgist to the possibilities of zirconia.

In the year 1788 the German metallurgist M. H. Klaproth, while engaged in the analysis of the mineral zircon, discovered that apparently 68 per cent of the mineral consisted of a very inert substance differing in its properties from all other substances known at that time, and which he ultimately determined to be the oxide of a new element. Having been first recognised in the mineral zircon, the name zirconium was proposed and ultimately adopted.

The element zirconium in the free state occurs in three forms—amorphous, crystalline, and graphitic. It has a density of 6.4 in the crystalline form, with a melting-point of about 2350° C. As the element has no important use in its uncombined state at the present time we will not dwell further upon its properties. It is not as rare as commonly supposed, having been determined by careful calculation to constitute 0.03 per cent of the lithosphere, about as plentiful as the element carbon ("Data of Geochemistry," F. W. Clarke, *Bul.* 491, U.S. Geological Survey).

Sources.—At the present time there are only two known minerals which occur in sufficient quantities to be considered as commercial sources of zirconium. The first of these is the natural oxide zirconia; the second zircon, or the silicate. As zirconium oxide is generally the starting-point for all zirconium compounds, the natural oxide is thus more eminently fitted as a commercial source than zircon. As found in nature, natural zirconia carries about 84 per cent of the pure oxide, with about 8 per cent silica and 3 per cent iron oxide. There are several methods in vogue for the extraction of the pure oxide, the best known being that of fusing the natural substance with sodium carbonate or hydroxide, thus producing sodium zirconate, which on being leached is hydrolysed, forming soluble sodium silicate and insoluble zirconium hydroxide. The precipitate after thorough washing can be readily converted into soluble salts by treating with any of the strong mineral acids.

Refractory Properties of the Pure Oxide.—Refined zirconia is a pure white substance, having a density of about 5 and a melting-point of 3000° C., according to Weiss. The first important use found for the oxide was to replace the calcium oxide cylinders used in the Drummond or so-called limelight. The great objection to the calcium oxide was its rapid deterioration, owing to its absorption of moisture and carbon dioxide from the air. Besides giving a more intense illumination, zirconium oxide was absolutely unaffected by moisture or any of the atmospheric gases.

Later, in 1880, R. von Welsbach impregnated loosely woven cotton or linen fabric with zirconium nitrate, securing a skeleton of zirconium oxide by incineration. The form of the fabric, thus perfectly preserved, became highly incandescent when heated in the flame of an ordinary Bunsen burner. Subsequent experiments proved, however, that thorium gave the same results at a much lower temperature; therefore it has almost entirely replaced zirconium for this purpose. These experiments of von Welsbach mark the inception of the incandescent gas mantle industry.

The next important application of the pure oxide occurred in 1897 in the Nernst light, developed through the behaviour of certain refractory oxides, which, when heated to a high temperature, become excellent conductors of electricity, and glow with an intense white light. This lamp consists essentially of a number of small rods or "glowers," composed of magnesia, zirconia, and yttria. By a suitable heating device the glower is raised to a temperature of 634° C., at which point current begins to flow, raising the oxides to incandescence. As the quantity of zirconia used in the Nernst lamp is comparatively small no great commercial application can be looked for in this quarter.

The remarkable heat-resisting qualities of zirconia at once commended it as a refractory of the first order. Its high melting-point, low coefficient of expansion, and low thermal conductivity make it apparently the ideal lining for electric furnaces of the arc type. The pure oxide, owing to the comparatively high cost of extraction, is too costly a material for industrial uses on a large scale. Careful tests have shown, however, that natural zirconia is eminently fitted for such work, and has only a slightly lower efficiency.

Very remarkable heat-resisting ware, such as crucibles, muffles, pyrometer tubes, combustion boats, and resistance cores for electric furnaces, can be manufactured from pure zirconium oxide mixed with from 3 per cent to 10 per cent magnesia, using starch, phosphoric acid, glycerin, or borates as binders. The ware is dried for several days at a low temperature, and then fired in the electric furnace at a temperature ranging from 2000° to 2300° C. This ware is practically impervious to liquids, and is not affected by strong acids or alkali fusion mixtures.

Owing to the extremely low coefficient of expansion zirconia ware can be subjected to very sudden changes of temperature, such as plunging a red-hot crucible in water, without the slightest danger of fracture.

The fusing-point of tungsten alloys and the boiling-point of pure iron, according to recent investigations, have been successfully determined in zirconia crucibles (Ruff, Lieferheld, and Bruschke, *Zeit. Anorg. Chem.*, 1914, 389).

The cost of the pure oxide for the manufacture of such articles as the foregoing and other ware requiring a maximum resistance to heat and corrosive action is at the present time not prohibitive, as it can be readily prepared from the natural zirconia by the method already briefly outlined. An iron-free oxide can also be prepared, according to a recent process, at a low cost (German patent No. 262,009). The pure oxide, mixed with sufficient sodium silicate or phosphoric acid to form a plastic mass, affords a cement or lute capable of withstanding the severe temperatures of electric furnaces of either the resistance or arc type.

Refractory Properties of Natural Zirconia.—To compete with the various high-grade refractory bodies now used industrially zirconia must possess certain superior properties lacking in these cheaper refractories, such as a higher melting-point or greater resistance to chemical agencies. In other words, the initial cost of a zirconia lining, which is rather high as compared with, for example, magnesite brick, is more than offset by its high melting-point (3200° F. to 3600° F.), high resistance to corrosive slags, metals, or metallic oxides, low thermal conductivity, and low coefficient of expansion. All of these superior factors indicate the life of a zirconia lining to be of very much greater duration than the best natural refractory lining now available.

Actual working tests made on a Martin-Siemens furnace in a steel works at Remscheid, Germany (private communication), using a zirconia-lined hearth, show that after four months of continuous operation at high temperatures the hearth was still in good condition, and would serve at least four months longer before renewal. Careful statistics compiled from these tests show a saving of 50 per cent in actual maintenance costs in favour of the zirconia lining over an ordinary refractory lining, such as is generally used. No allowance was made for increased production and higher efficiency. Owing to the low thermal conductivity of zirconia (about one-half that of ordinary firebrick), it has been demonstrated in actual practice that a two-inch lining is equivalent to four-inch of chamotte.

The high resistance of this refractory to such metals and alloys as copper, steel, bronze, and red brass should commend its use in their metallurgy. Gaseous or molten fluorides affect it markedly, however, likewise bisulphates, but as there are only a few substances inert to such corrosive compounds, this can be hardly cited as a detrimental feature.

As a protective coating or paint for ordinary fire-brick exposed to the destructive action of acid fumes or slags zirconia should find a limited application.

A suitable bonding medium for such a purpose might be found in a weak solution of water-glass or sodium silicate.

All bonding materials must be used advisedly, as they naturally tend to lower the fusing-point of the refractory. In lining furnaces or other metallurgical apparatus, natural zirconia can be mixed with water-free tar as a binder, in which case wooden forms are generally used. These are allowed to remain in place and consumed during the initial heat. The temperature should be raised very slowly at first to eliminate the volatile products in the tar, after which a temperature of at least 1400° C. must be maintained for about forty-eight hours. Natural zirconia begins to fuse at about 1800° C., and at 2000° C. there is a noticeable volatilisation of silica and other impurities.

In the manufacture of natural zirconia, brick, muffles, crucibles, and small articles of refractory ware about 2 per cent of air-slaked lime as a binder has been used with success. In practice, a batch composed of 75 per cent 100-mesh zirconia, 23 per cent of 10-mesh, and 2 per cent of slaked lime is worked into a plastic with a 3 per cent solution of 38° Bé. sodium silicate. The bricks or ware are then pressed from this and allowed to thoroughly dry in a warm atmosphere. The procedure from this point on is the same as in the burning of ordinary refractories, except that a temperature of at least 1400° C. is necessary to secure the proper vitrification.

As the density of zirconia is rather high (about 4.2), it has been suggested, where imperviousness is not desired, that the incorporation of certain organic substances or volatile salts, which would be destroyed during firing, thus producing small air cells, might serve to lighten the finished product without impairing its efficiency. Sawdust, cork dust, or certain ammonium salts might prove of value for such aeration.

The low coefficient of expansion renders zirconia ware free from all danger of fracture due to sudden changes of temperature. In this respect it resembles fused silica ware.

The cost of zirconia as compared to certain artificial refractories produced in the electric furnace is considerably lower, which, in view of its remarkable properties, should commend it strongly to the furnace man or metallurgist.—*Metallurgical and Chemical Engineering*, xii., No. 12, 791.

COLLOIDAL GRAPHITE LUBRICATION.

By W. W. ACHESON, Jun.

RECENTLY, in a conversation with the author, the consulting engineer of the largest paper mill interests in Wisconsin remarked:—"I have been connected with this company for thirty-seven years, rising from an operator to the position of general superintendent. In this present position, until the last year or two, I have thought that any employé capable of walking about with an oil-can was good enough to oil machinery. I now see this is a very grave mistake, for oiling machinery requires intelligence and training. The idea of placing a cheap labourer in the position of caring for expensive machinery is a vital mistake." This point, though well known to men who have studied the subject, is very difficult to bring to the attention of the management of industries. To oil machinery properly it requires an intelligent man who *thinks* what he is doing, applies the *right* amount of the *right* oil at the *right* time and in the *right* way.

In order to adequately cover this subject it seems best to give illustrations of some conditions that are of daily occurrence and that seldom come to the attention of the heads of manufacturing departments. The following incident is typical:—

Joe was a licensed engineer, looked upon as a capable man in his profession. He was placed in charge of a new power plant. After operating his engine for several weeks he found that the cylinder was not getting the lubrication necessary, and cutting was beginning to take place. The quality of the oil used was good; in fact, this oil was costing his "boss" 55 cents per gallon. Joe would not go to the "boss" with his troubles, being afraid his job might be taken away from him. On the other side of the city a friend of Joe's was the chief operating engineer of a large central lighting plant, so Joe made excuses for a trip down town, and went to consult with his friend, Fred. Now the first questions that Fred asked, after Joe had told his troubles, were:—

"Are you using dry or saturated steam?"

"What is the steam pressure carried in your boiler?"

"What is the piston speed of your engine?"

"What is the nature of the boiler compound you are using?"

"Is your engine working to capacity or half-load?"

When Joe had answered these and several other questions, and, by the way, he had to return to his plant to get the answer to most of them, then Fred said:—

"Your trouble is that you are using too *good* an oil. Get a cheap heavy black oil, about the cheapest thing you can find, and use it one drop every two complete revolutions of the engine. Do this and you will get the results you desire."

This is simply one illustration of the necessity of selecting a lubricant suitable to the requirements, for to attempt to use the same oils for every class of lubrication in a plant is folly, and shows ignorance of one's work. A selection of the proper oil for each class of machinery to be lubricated is necessary if one wants to produce shop efficiency and economy. A high speed bearing will require a different lubricant than that required by one moving slowly and doing heavy duty.

Not so long ago the author was in a sugar mill watching seven men attempting to operate a "hog" for the grinding of cane. Now they had been endeavouring for better than two weeks to make this machine run. They had tried

every lubricant obtainable, and even had piped running water to each of the journals, and yet the best they could get was about twenty minutes running, when the journals would become heated to the melting-point. They removed the babbit, and re-poured the bearings with new metal, and still it ran hot. In watching these men endeavouring to make this machine run it seemed that its speed was excessive. By means of an indicator it was quickly determined that the speed was 218 rev. per min. above the running time recommended by the manufacturer. In this case a heavy roughly constructed machine was being run at a higher speed than its journals could stand. Upon changing the driver this hog ran very well, and no more heated journals were had. Nevertheless, the company had lost several hundred dollars in experimentation.

Aside from selecting an oil, it is necessary to have the working conditions as nearly correct as possible. Neither oils, nor greases, nor colloidal graphite, nor anything else in the way of lubricants will correct a mechanical difficulty. But, when your working conditions are as they should be, then the addition of colloidal graphite to the ordinary lubricants will reduce friction by more than 20 per cent.

Colloidal graphite was invented by Dr. E. G. Acheson, who in 1897 first produced artificial graphite on a commercial scale. While carrying on experiments with carborundum in an electric furnace, he noticed that when the substance was brought to a temperature far beyond that of its production, decomposition occurred, and the silicon portion of the carborundum dissipated as volatile matter, while the carbon proportion remained as pure graphite. It now requires two plants which have a total equipment of about 9000 hp. to supply the demand for graphite. This is being shipped to all parts of the world, the consumption in 1913 being 16,000,000 lbs.

Graphite is manufactured in electric furnaces which are under perfect control and which reach a temperature of 7500° F., so that all substances except carbon are volatilised. The remaining carbon is thus extremely pure, and is entirely converted into graphite. In fact, entire furnace loads have proven to contain more than 99.90 per cent pure graphite carbon. The small amount of non-graphitic material consists of condensed mineral gases collected during the cooling of the furnace. Since the power is at all times under absolute control the entire process is flexible, so that any quality of graphite desired can be produced by varying the raw material used, the method of running the furnace, and the amount of power expended.

After this chemically pure graphite is produced in the electric furnace it is then reduced by a process of disintegration, and passed through a sieve having 40,000 meshes to the square inch. The resulting powder is much finer than the finest flour, but not reduced to a condition where it can be employed in connection with oils as a lubricant. In order to secure a still finer subdivision this disintegrated graphite is subjected to a treatment called "deflocculation." This consists in a mastication of the disintegrated graphite with a water solution of tannin, the amount of tannin being 6 per cent by weight of the amount of graphite being treated. The tannin enters into and explodes the individual particles of the disintegrated graphite to a condition approximately 1000 times finer than their original state. To give a clearer idea we will say that disintegrated graphite is of such fineness that it takes 338 particles to cover the distance of 1 inch, when these particles are placed side by side; after the tannin treatment the resulting deflocculated graphite is of such fineness that it requires 338,704 particles to cover the distance of 1 inch. This reduction in lineal dimensions means a reduction of cubical volume corresponding to the cube of 1000, or the ratio of the size of the individual particles is as one drop of water is to 264 barrels of water.

Graphite in this condition of fineness is on the market under the trade name of "Oildag"; O-I-L plus deflocculated Acheson graphite, and is being used in every class of lubrication.

Oil containing colloidal graphite (deflocculated graphite is now being aptly termed colloidal and liquid graphite) constitutes a most dependable form of lubricant. When introduced into a bearing the graphite particles, being infinitesimal, penetrate the pores of the metal. These particles accumulate until the surfaces in contact are completely amalgamated with a thin veneer which has been termed a graphoid surface. This film, unlike that of oil, is free from intrinsic friction and exceedingly stable in its construction, being capable of withstanding far greater pressure than any form of hydrocarbon regardless of its viscosity.

The graphoid surface not only greatly reduces friction but practically eliminates wear. So lubric is the nature of this graphite film that upon its establishment oil consumption may be considerably reduced. It has been recorded that one-sixteenth less oil is necessary when colloidal graphite has been used. If the oil supply of a bearing is either accidentally discontinued or completely consumed, the original graphoid surface alone will hold up as a lubricant for a long time, preventing a hot bearing.

It has been found, after many exhaustive tests, that 0.35 per cent of colloidal graphite properly diffused in oil is sufficient.

Colloidal graphite in gas-engine lubrication possesses many advantages over plain oil. The formation of carbon deposits in cylinders results from the inability of the piston rings to effect a thorough wiping back of the lubricating oil, so that a portion remains in the cylinder and is decomposed. This source of trouble usually ceases with the use of colloidal graphite. The minute particles of the graphite enter the interstices of the metal, and form a soft unctuous film that is not attainable by any mechanical operation.

With the establishment of this film or amalgamation of graphite upon the cylinders, and upon the face and sides of the rings, there is effected a perfect fit between the walls of the cylinders and the rings, due largely to the freer action of the rings in their grooves. This fit produces or causes a clean wiping back of the excess oil after each splash, so there remains no oil to decompose and produce carbon. What carbon deposits there may be formed will be found to be of a nature similar to damp lamp-black, and may be wiped off clean. There will be an entire absence of the hard burned carbon that causes cylinder troubles.

Dr. C. H. Benjamin, now dean of Purdue University, while he was with the Case School of Applied Science of Cleveland, Ohio, made a number of tests with colloidal graphite. One of his trials was made on a journal having a pressure 125 lbs. per square inch, and running 445 rev. per min. This test was made using the same oil and same rate of feed for two runs, all conditions identical, excepting that colloidal graphite was added to the oil in one run. A lower coefficient of friction was very noticeable with the addition of the graphite. After two hours' lubrication with the oil, the feed was shut off while the bearing was permitted to run, and within ten minutes the lubrication from the oil failed, producing an abrupt rise in friction, which necessitated stopping the run. By the addition of colloidal graphite to the same oil for a period of two hours before shutting off the feed, there resulted an almost perfect lubrication over the time of one hour and twenty minutes, thus showing that the graphite is dependable as a lubricant when the oil feed is cut off.

Another interesting experiment was conducted by Dr. Chas. F. Mabery of the Case School of Applied Science. He also shut off the oil feed after two hours, and let the journal run. In just nineteen minutes the plain oil lubrication failed absolutely, while the same oil carrying colloidal graphite gave a perfect lubrication for four hours after the feed had been cut off. In this test Dr. Mabery used a pressure of 200 lbs. per square inch and 450 rev. per min.

There remains one more point worthy of mention.

Colloidal graphite, being molecular, refuses to associate with an acid or alkaline oil. Some of the oil refineries use the acid process to precipitate the colouring matter or heavy carbons that are present in oils, and then fail to remove all this acid. Every oil to be a good lubricant should be neutral. The presence of acids, in any appreciable quantities in oil, detracts from their lubricating value. A very simple and very positive test for the presence of acid in oil is to take a 2-oz. bottle of the oil, and thoroughly mix, say, 30 drops of "Oildag" with this amount, and allow the mixture to stand undisturbed for two to five days. If the oil is neutral there will be no sign of precipitating of the colloidal graphite. Should there be a decided precipitation then the oil is acid, and therefore is not the best to be desired for lubrication. If graphite is not carried in diffusion, but caused to settle out of the oil, then it ceases to be colloidal graphite. A colloid, being a solid in suspension but not in solution, cannot be precipitated.—*Chemical Engineer*, xxi., No. 3.

EDUCATION FOR RESEARCH.*

By W. H. WALKER.

THE general disturbance in the chemical and pharmaceutical market occasioned by the present European war has sharply emphasised the dependence of many American industries upon the supply of both raw and finished material obtained from abroad. The public is asking the pertinent questions, Why must we import so large a proportion of our coal-tar dyestuffs when we have so much highly coloured coal-tar at home? Why do we depend upon Germany for lithia salts when all the lithium-bearing minerals come from America? Why has a European war increased the price of articles not in any way connected with the war?

It is a principle of pedagogy that to insure the best results when giving instruction it is necessary to create a receptive attitude on the part of the student—to encourage an inquiring frame of mind. To-day there is a keener and broader interest among manufacturers than ever before in determining those factors which have been controlling in giving European nations an advantage in many lines of industry which it would seem the United States is in every way equally fitted to enjoy. The public now possesses that desirable receptive attitude and inquiring frame of mind. It would seem, therefore, that the present is a psychological moment for a campaign of education which would benefit the chemical profession directly and the entire community indirectly.

A number of very important factors in successful chemical industry have already been considered by this audience, and your able Committee has reported its findings and recommendations regarding a so-called anti-dumping clause, an adequate protective tariff, and the United States patent law. There are, however, some very general matters bearing upon the subject that may be profitably considered. First, there is the necessity for further education of the public. Notwithstanding all that has thus far been done the public is as a whole ignorant of what a chemist professionally is and the place he occupies in the community. A great many people do not yet distinguish between a chemist and an apothecary, or between the latter and a dispenser of soda water. A chemical engineer is frequently visualised as a man who runs a so-called chemical fire-engine. And yet this same public will talk volubly about the position occupied by Germany in the industrial chemical world, and ascribe untold advantages to systems of education and industry which it does not understand. The magnificence of German chemical

industry has been compared to the chemical industry of America almost *ad nauseam*. Generally the inequalities are greatly exaggerated, and many may be explained without any discredit to the American profession. We are wont to instance the telegraph, the sewing-machine, the electric light, and such developments when desiring to find compensating achievements to offset the contributions of Germany to chemical science, but we forget that the sulphite process for obtaining cellulose from wood, the chromium process for leather, calcium carbide, carborundum, and many other chemical industries owe their origin and development to American chemical genius. Nothing succeeds like success, and while we should continue to learn from Germany the many things which she is in a position to teach us, we must cease making unfair comparisons and root for the home team.

The increasing appreciation with which the chemically trained man is held by the American manufacturer argues well for the future. Not many years ago if a chemist was employed at all it was simply and only for so-called control work. The manufacturer was satisfied if he maintained his standard and turned out a uniform product. There was little inclination to risk money by placing on the market a new product. There has been an encouraging change within the last ten years, and the manufacturing public is awakening to the desirability of progress in both the quality of his product and the methods of his plant, and he is beginning to realise that a man trained in experimental science is a necessary addition to his organisation. But the average manufacturer of America still expects bricks without straw. To cite an example of what I mean. A large shoe machinery company known to us thinks nothing of allowing a skilled mechanic two or three years in which to perfect a desired movement or correlation of parts of a machine, yet this same company was keenly disappointed, even disgusted, because a skilled chemist did not produce in six weeks a special alloy with sharply defined properties. In one case the solution depended upon mechanics which the superintendent understood and could see, while in the other it was chemistry which he did not understand and the action of which he could not follow.

The manufacturer of to-day is beginning to be strongly attracted by the terms "research" and "research department." He has a sort of conviction that by adding such an appendage to his organisation he will be insured of progress and will protect himself from difficulties, much in the same way that a good vaccination mark insures against smallpox.

My plea at this time is not so much for greater generosity on the part of the employer in matters of laboratory facilities, special equipment, or a good library, however important these are, but rather for a larger appreciation of the conditions which make for ultimate success in research work. Among these conditions may be mentioned, first, the choice of the research worker. I am satisfied that no little harm is done the cause of industrial research by the employment of immature, untrained men, who pass as men skilled in science, but who either know no science or who have had no experience in that very difficult art of applying science to industry. The harm comes not so much because the particular investigation fails, but rather because the management believes it has shown that its problems are not susceptible to solution by scientific research or amenable to the aid which applied science can render. This unfortunate condition is frequently brought about by false economy on the part of the management. A research chemist should in its opinion be obtained with the ease and salary of an apothecary's clerk. A horse suitable for drawing an ice cart is bought and expected to win a Derby.

Another mistake frequently made is in the organization of the research staff, or, if done on a less pretentious scale, the research work. Investigation work should never be allowed to interfere with factory production. The average mill superintendent quickly

* Address at the Joint Meeting of the New York Sections of the American Chemical Society, the Society of Chemical Industry, and the American Electrochemical Society, Chemists' Club, December 11, 1914. From the *Journal of Industrial and Engineering Chemistry*, 1915, vii., No. 1.

becomes antagonistic to anything which cuts down his output. Yet it is not infrequently the case that a research assistant is placed directly under such a superintendent, and may even report to him exclusively. The superintendent may have won his position on account of his ability to get the maximum of work out of his men, and may have risen in spite of an extreme narrowness of vision rather than on account of his breadth of view. Or, again, the research man may be at the beck and call of the production department, and thus be constantly taken away from his real task to do routine testing of the product; or, the purchasing department may have the right to demand such of his time as may be necessary to check up specifications and purchases made thereunder. Continuous concentrated effort is essential to a successful investigation, and the organisation of such work should insure freedom from serious interruption of any kind.

A further tendency on the part of the employer is to expect positive results as soon as the work is well under way; having planted the seed he is impatient to harvest the crop. At best experimental work is slow, and this fact must be cheerfully accepted at the beginning. When considering the large amount of research work done in Germany we forget the great number of men who are there engaged in investigations of every possible type. If we had some means of determining the average yearly output per man I am sure we would find it extremely small. It is my belief that the *per capita* return for research work is greater in America than it is in Germany. It is only when the results of each individual are multiplied by the great number of men in the work that the enviable amount of scientific work produced yearly in Germany is reached.

(To be continued).

CITY AND GUILDS OF LONDON INSTITUTE.

TECHNICAL TRAINING.

THERE can be no doubt that when the immediate European crisis is over there will be a great demand in British industrial circles for young men who have received a good technical and scientific training in engineering, mechanical and electrical, and in chemistry.

Manufacturers of chemical products and constructors of engineering machinery of all kinds should make strenuous preparations to meet the demands of expanding trade, but their efforts will be largely in vain unless they can count on a supply of young men thoroughly trained in the principles of science and in their technical applications.

Brains will count in the successful competition for supplying the markets of the world with those products which depend on science for their manufacture. It is not enough to have skilled workers; scientific training is nowadays an absolute essential.

Prospects in the Chemical Industries.—The present war has enabled the people of this country to realise the extent to which foreign competition has successfully attacked many of our industries. In certain branches of chemical industry, and more especially those dependent upon organic chemistry, such as dyestuffs and colouring matters, synthetic drugs, &c., the failure of supplies from the Continent threatens to cripple many of our manufactures and to throw large numbers of men out of employment. The Board of Trade, aided by a body of expert advisers, is endeavouring to promote the development of new branches of industry here, in order to remedy the state of affairs. In view of the circumstance that the development of these industries abroad has been entirely due to the recognition by our competitors of the importance of the bearing of science and technical education upon industry, it is to be hoped that our manufacturers will now rise to the opportunities which are offered to them through the suspension of foreign manufacture and the suspension of patent rights held by the enemies of the Crown. If, as is anticipated, new branches of chemical industry are estab-

lished in this country, the chances of successful careers for technically trained chemists are certain to be more numerous and the demand for such men greater than at any other period of our industrial history. The students trained in the chemical laboratories of the City and Guilds Technical College, Finsbury, have firmly established the reputation of the college for their ability to enter upon industrial work and to advance the scientific side of manufacturing chemistry. Many of them have contributed and are continuing to contribute valuable original researches, both in theoretical and technical chemistry.

Prospects in Engineering.—During the last decade large contracts for the supplying of iron and steel work for railway construction, bridges, and the like, which ought never to have left our own manufacturers, have been secured by their foreign competitors. In addition to these large supplies of machinery, railway rolling stock, machines for quick repetition work, and of cheap machine tools (although of inferior quality) have been made on the Continent and supplied to our colonies. It is very clear that as soon as the war is finished the civil and mechanical engineer will be required to restore all the old means of transport, and thus in two or three years' time there should be a general expansion of the mechanical and engineering trades, and as a result many openings for properly trained young engineers. Business articles recently printed in the *Times Engineering Supplement* show the magnitude of German machinery exports. Should English capitalists lay down plant in order to regain this trade, the men equipped with the best scientific and practical training should be at hand ready to play their part in the recapture and holding of trade which should never have left us. Such men will be needed. The training of such men in science is our work. The engineering laboratories, mechanical and electrical, of the City and Guilds Technical College, Finsbury, are well equipped for the training of engineering students. The testing of materials and plant, the efficiency of engines and electric motors of all kinds, heat testing, fuel testing, hydraulic engineering, structural engineering, electric lighting, and the electric transmission of power, are all taught in laboratories designed for the purpose. The electrical laboratories at Finsbury were the earliest to be equipped in London for the purposes of technical training in electric light and power. They have been extended and remodelled from time to time, and there have been numerous recent additions to their equipment. The design of electrical machinery has been taught with conspicuous success for over thirty years.

Courses of Training.—I. Mechanical and Civil Engineering, under Prof. A. J. Margetson, B.Sc., M.A., M.Inst.M.E.; II. Electrical Engineering, under Prof. Silvanus P. Thompson, D.Sc., F.R.S.; III. Chemistry, under Prof. Raphael Meldola, D.Sc., F.R.S. The full course leading to the diploma of Associateship (A.C.G.F.C.) is a three years' course for matriculated students. For non-matriculated students there are shorter courses of two (or three) years, leading to the Certificate of the college. The fees are £20 per annum, payable in advance.

For the programme of the College and all information as to educational matters, and as to fees, scholarships, &c., apply to the Principal, Prof. SILVANUS P. THOMPSON, D.Sc., F.R.S., or to the Registrar, City and Guilds Technical College, Finsbury, Leonard Street, City Road, London, E.C.

*Biochemical Synthesis of α -Mono-*d*-galactoside of Ethylenic Glycol.*—Em. Bourquelot, M. Bridel, and A. Aubry.—The α -monogalactoside of ethylenic glycol can be obtained by dissolving galactose in water and adding glycol and then yeast. The rotation of the solution increased $8^{\circ} 32'$ in nine months. The galactoside consists of colourless needles with a slightly sweet taste. It is soluble in water and in alcohol, and does not reduce cupropotassic liquid.—*Comptes Rendus*, clx., No. 21.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, June 25, 1915.

Dr. A. RUSSELL, M.A., Vice-President, in the Chair.

A PAPER, entitled "*Conduction of Electricity Through Metals*," was read by the President, Sir J. J. THOMSON, O.M., F.R.S.

The discovery by Kamerlingh Onnes, that at the temperature of liquid helium some metals can exist in a state in which their specific resistance is less than one hundred thousand millionth part of that at 0°C., appears to necessitate the abandonment of the ordinary theory of metallic conduction, as the experimental conditions prohibit the explanation of the phenomenon by an abnormal increase, either in the number or mean free path of the free electrons. The effects observed by Kamerlingh Onnes may, however, be accounted for by a theory of metallic conduction previously given by the author in "*The Corpuscular Theory of Matter*." On this theory the atoms of some substances contain electrical doublets—i.e., pairs of equal and opposite electrical charges at a small distance apart. The effect of an applied E.M.F. is to alter the heterogeneous distribution of the axes of these doublets by bringing them into partial alignment with the field. The influences preventing complete alignment are considered, and it is shown that if M is the moment of a doublet, N the number per unit volume, w the average kinetic energy of the molecules ($=R\theta$, except at very low temperatures), and I is the resultant of the molecular moments in the direction of X the electric force on the doublets, then—

$$I = NMf(XM/w) = NMf(x), \dots \dots \dots 1$$

in which $f(x) = 0$ when $x = 0$, and $f(x) = \infty$ when x is infinite.

X is made up of the applied electric field X_0 plus an internal field due to the polarised doublets, the latter of which is assumed to be proportional to I . Hence, $X = X_0 + kI$, and $x = M(X_0 + kI)/w$, or—

$$I = wx/Mk - X_0/k \dots \dots \dots 2.$$

For any value of X_0 the value of I can be found from the intercept of the straight line (2) with the curve (1). The effects due to any value of I will be the same as if I doublets per unit volume pointed in the direction of the field, the axes of the rest being uniformly distributed in all directions, and the substance may be pictured as containing a number of chains of polarised atoms whose doublets all point in the direction of the field. The electrons in the atoms will be acted on by forces due to the neighbouring polarised atoms, and the theory supposes that in conductors the electrons are easily abstracted by these forces from the atoms to which they are attached, and pass, under their influence, from atom to atom round the polarised chain. If p electrons pass along each chain per second, and if there are n chains per square centimetre perpendicular to the field, the current density $i = epn$, where e is the electronic charge. It is shown that p is independent of X_0 , and so the ratio of i to X_0 will follow the same laws as that of I to X_0 .

When w/Mk is large, as at ordinary temperatures, the slope of (2) will be steep and will intersect (1) near the origin where it approximates to a straight line. In these circumstances it is shown that Ohm's law holds. As the temperature falls the slope of (2) also decreases, and may ultimately become less than that of the tangent at the origin of (1). In this case, if we start with an external field producing a polarisation, I , and gradually reduce the field to zero, the point of intersection of (1) and (2) moves along the former, but still gives a finite value of I , when (1) passes through the origin—i.e., when $X_0 = 0$ —and a current continues to flow in the absence of an applied E.M.F. as observed in one of Kamerlingh Onnes' experiments.

On this view, therefore, the function of the applied field is to produce the alignment of the doublets; the actual transference of electricity is effected by the large inter-atomic forces brought into being by the polarisation of the doublets. Thus, if the polarisation remains on withdrawing the applied E.M.F. the current will also remain.

In addition to the disturbing effects on the chains due to thermal energy, there may be mutually directive action between different atoms such as gives rise to crystallisation. The effect of this is considered, and it is shown that if this factor is large the metal cannot become superconducting.

Prof. S. P. THOMPSON, in proposing a vote of thanks to the President for his paper, said there were one or two points which he had not quite grasped in the course of the lecture, and which he would like to have cleared up. We were asked to assume a ring of polarised atoms with positive and negative sides producing an electric force which caused the transference of electrons from one atom to the next and so on round the circuit, this transference constituting the electric current. Although the responsible factor in the transference of the electrons was the internal force, an external force was necessary to produce this, and he did not see why, on withdrawing the applied field the process should go on instead of stopping after one, or, at most a few, transfers had taken place. Were there any physical grounds for supposing that the forces of restitution were greater in the case of mixed crystals than in homogeneous ones? Lastly, he did not see the physical necessity of introducing the quantity d . Could the total force of restitution from all causes not have been included in a single symbol?

The PRESIDENT, replying to the points raised by Prof. Thompson, said that the energy was not spent in the movements of the electrons, but in creating the initial polarisation, and if, in any circumstances, this could be maintained, the current would go on without any loss of energy, except a little by radiation. The formation of mixed crystals of A and B was due to the force between a molecule of A and one of B being greater than that between two of A or two of B. Hence, the force of restitution called into play on displacing a molecule will be greater in the case of the mixture than in that of the pure metals. He had thought it better to denote the force of restitution due to the directive action of neighbouring molecules, which did not depend much on temperature, by a separate symbol d , and keep it clear from the restoring couple due to the gyrostatic action which did depend on the thermal conditions.

A paper "*On an Unbroken Alternating Current for Cable Telegraphy*," was read by Lieut.-Colonel G. O. SQUIER, Ph.D.

1. The paper proposes a new angle of view in the method of transmission of signals in the submarine telegraph cable, and describes some apparatus for operating on the general principles involved.

2. An ocean cable is considered as a power line, and starting with the standard form of circuit which would be used in case it were required to operate an electric motor through an ocean cable, experiments are described to determine the minimum possible variations required in such a circuit to permit the alternating current received to be interpreted in dots, dashes, and spaces of the present alphabet. The uninterrupted alternating current used in transmission is operated on synchronously by the ordinary transmitting tape, so as to alter the impedance of the transmitting circuit at the instants when the current is naturally zero. Dots, dashes, and spaces are each sent by semi-waves of either sign, but of different amplitudes. The alternating current received may be read directly from the record made by a syphon recorder, or this current may be employed to operate a syphon Morse printer, by means of an adaptation of Muirhead's gold-wire relay, or a Heurtley magnifier and a local wire relay.

3. The voltage stress along an Atlantic cable when an

alternator is employed is shown, and the transmitting impedance of such a cable is computed as the frequency varies.

4. A special form of cable dynamo to operate at frequencies from 4 to 10 was used in the experiments described.

5. The fundamental principle is developed of never metallically "breaking" the transmitter circuit, which permits of greater accuracy in balancing the duplex bridge.

DISCUSSION.

Mr. W. DUDELL said the author and Dr. Crehore some 20 years ago were trying to get rid of the square corners of the waves due to the upper harmonics. The difficulties now appeared to have been entirely surmounted. As pointed out in the paper, if the current be broken the harmonics are again introduced, and he thought the method of avoiding this by exact synchronism of the transmitter and generator very ingenious.

Prof. S. P. THOMPSON thought the great merit of the method of working was that it reduced everything to the sine curve. Anything else than a sine curve was less economical financially and electrically. He admired the author's method of obtaining synchronism and of making the alterations in amplitude exactly at the zero points.

Mr. A. CAMPBELL said that frequencies of 4 to 10 seemed to be usually employed. What were the limits of frequency practically possible on an Atlantic cable, for example? Was the limit set by the facility with which the signals could be read by the operator?

Dr. H. W. MALCOLM thought that by adopting the principle of never breaking the circuit the author was working on the right lines. The distortion in a long cable was so great that the wave-form of the signal received depended very little on the form transmitted, and so the wave-form could be chosen to produce the least disturbance at the transmitting end. For this the use of a series inductance was helpful. Another method was to use a commutator to shut off the recorder while the battery circuit was made or broken.

Prof. G. W. O. HOWE asked why the amplitude of the current which passed between signals could not be made zero. Was it an instrumental difficulty, or was there a theoretical advantage in having it large.

The AUTHOR, in reply, said it was desirable to have the amplitude large between signals, so as to depart as little as was practicable from its ideal sine wave. Moreover, the energy was utilised to feed the tape. With regard to frequency, 10 was very high from a cable standpoint, but he was hopeful that when the physicist had attended to the problem of the receiving instrument, much higher frequencies, say within the aural limit, would be possible.

NOTICES OF BOOKS.

Surface Tension and Surface Energy and their Influence on Chemical Phenomena. By R. S. WILLOWS, M.A., D.Sc., and E. HATSCHEK. London: J. and A. Churchill. 1915.

THE lectures contained in this book were delivered by one of the authors at the Sir John Cass Technical Institute, and the text of them first appeared in the *Chemical World*. The lecturer aimed at giving an outline of general principles rather than going fully into experimental details, and he succeeded in producing a clear summary in which the explanations and illustrations are always graphically put. The great difficulties of treating the subject at all adequately without introducing a good deal of mathematics have been surmounted, and the reader will be able to get from the book a good working knowledge of the phenomena of surface tension and surface energy, even if his

knowledge of mathematics is only very limited. After a discussion of the basal laws the authors proceed to the consideration of the relations which have been established between surface tension and physical constants, and between surface tension and chemical constants, and the experimental work which has been done in the investigation of these relations is admirably reviewed. No references to original literature are given, and the book is essentially one for readers who are specialising in colloidal chemistry, and who do not wish to read through many descriptions of experimental work or discussions of points of theoretical interest only.

Experimental Electricity and Magnetism. By M. FINN, M.Sc. (Dunelm.). London: G. Bell and Sons, Ltd. 1915.

IN this experimental course of electricity and magnetism the student uses as his source of current the electric lighting supply of the laboratory, and in the first lesson studies the resistance, potential, and heating effects of a circuit of constant E.M.F. He then goes on to practical work with magnets, magnetic induction, and the earth's horizontal magnetic field, and so passes to the magnetic measurement of the electric current. The chemical effects of the current and Ohm's law are then treated, and electrostatics is taken up last of all. The book is distinctly novel in many respects, and will be found valuable for the older boys in schools and for technical students. Young beginners might find the plunge into the middle of things in the very first chapter rather bewildering, but the experiments, especially those in magnetism, are likely to arouse a boy's interest and induce him to make the best use of his reasoning powers.

Notes on Dental Metallurgy. By W. BRUCE HEPBURN, L.D.S. (Glasgow). Second Edition. London: Baillière, Tindall, and Cox. 1915.

THE principles of the methods commonly adopted for extracting from their ores the metals which are used in dental work are well explained in this book, and the preparation of alloys and amalgams is described in considerable detail. The general dental practitioner will find the book particularly useful, giving as it does the composition of all the most valuable and widely used alloys and solders. In the second edition the whole text has been carefully revised, and a good many additions and improvements have been made. The chapter on alloys is contributed by Prof. Campion, of the Royal Technical College, Glasgow, and is quite new, and the chapter on dental amalgams has also been entirely re-written.

Volumetric Analysis. By A. J. BERRY, M.A. Cambridge: The University Press, 1915.

THIS book is intended to fill the gap between quite elementary works on volumetric analysis, in which only easy typical methods are described, and the standard treatises on the subject which are unsuitable for the use of students who have not been through a complete preliminary course. The theoretical aspects of volumetric work are emphasised, and an excellent discussion of the theory of indicators is provided. The actual experimental details are not usually given very fully, but the average student who has done some qualitative analysis should be able to carry out the determinations without additional help or explanation. At the end of the book some typical examples are given to show the magnitude of the errors which may be expected when ordinary uncalibrated measuring instruments are employed. The order in which the methods are described would not appear to be quite the best which could be adopted for students who had done no volumetric work previously, for processes involving the use of potassium permanganate, dichromate, &c., are given first, and acid and alkali titrations are postponed till quite the last.

THE CHEMICAL NEWS.

VOL. CXII., No. 2904.

MASS, WEIGHT, AND ELECTRICAL INERTIA.

By F. H. LORING.

MR. H. STANLEY REDGROVE'S interesting paper entitled "Matter, Mass, Weight" (CHEMICAL NEWS, cxii., 13) contains some criticisms of my article (CHEMICAL NEWS, cxi., 301) which calls for a reply in support of my arguments.

Mr. Redgrove objects to my definition of mass as quantity of matter, but the definition I gave is followed up by methods of measuring mass, and these of necessity involve quantities of matter which are in fact the basis of our knowledge of mechanics. The well-known illustration of the effort required to move a massive gate horizontally on practically frictionless hinges forcibly brings to notice the idea of quantity of matter quite apart from gravitational attraction. Mass need not be defined by weight (force of gravity) since its resistance to change of position or motion need not involve the action of gravity at all, as instanced by the gate, but ordinary mass involves quantity of matter; moreover, time comes into consideration when defining its quantity or amount by forcing it (the matter) to move, the time rate of change (acceleration) in velocity being a factor here as in the case of falling bodies. We thus have two different but really connected methods of arriving at the mass of a body. Mr. Redgrove, of course, admits practically all this, but questions the precise use of the words "matter" and "quantity," &c. (see below).

Experience has given us a conception of matter which, though difficult to define philosophically, enables us to compare different quantities and test out the relations involving force, acceleration, and mass. Whether we evade the ultimate issue by substituting names for matter makes no difference in my opinion.* Mr. Redgrove uses the word "body." Bodies are quantities of matter; at least in mechanics.

† We cannot discuss this subject properly without considering electrical inertia, or electromagnetic mass, in view of the advances since the time of Newton. Inasmuch as the electron has electromagnetic mass,† being a quantity of electricity, it has been regarded by some physicists as a fragment of matter; indeed, we use the word *particle* as a descriptive term—a term for discreteness. Sir J. J. Thomson (1914), however, tells us that we have not yet found out whether the electron has weight. Are we justified, therefore, in regarding manifestations of energy or certain entities that are isolatable and which have not been weighed as ordinary matter or mass in the Newtonian sense? Surely we are not justified in such a conclusion when discussing ordinary mechanical principles, such as the law of falling bodies, or the inertia of ordinary matter. It is, however, permissible to make excursions from beaten tracks and venture new ideas.

* Mathematicians often steer clear of debatable issues by avoiding words and using formulae, or such terms as have proper and restricted meaning, and certainly this is quite wise and legitimate, but sometimes we must think things out in our own way along simplified lines, and connected with experiences, if we want to really see where we are.

† In *Harper's Monthly Magazine* (1914, p. 566), Sir J. J. Thomson gives a remarkably clear short account of Cathode Rays, which are composed of or comprise "corpuscles" (= negative electrons) and Positive Rays (*Kanalstrahlen*). The Cathode Rays are deflected by superposed magnetic and electrostatic fields, and a parabolic registration (single parabola) is obtained on a photographic plate, from which is determined the electromagnetic mass of the individual particles (negative electrons) forming the rays. The value is $1/1700$ th of the ordinary mass of a hydrogen atom. This method corresponds in all essentials with the Positive-ray method, whereby certain atomic and molecular masses are ascertained independent of all chemical analysis; the latter method gives the well-known groups of parabolas, owing to the different gaseous chemical atoms and molecules present in the vacuum tube, or different charges "on" a given type of atom.

Mr. Redgrove would evidently have us believe that mass is not an absolute property, but that it is variable under extreme conditions, because Kaufmann has shown in a most brilliant experiment that the β -particle (negative electron) experiences a change of electromagnetic mass (increases) when its velocity becomes very great (see Lodge, "Electrons," 1910, chap. xiv., G. Bell and Sons). In my opinion it seems more rational to keep our ideas of matter as practically defined by gravitational or universal attraction intact from these newer ideas until more is known. We may, in the meantime, make it a *sine qua non* of matter that its mass is invariant; that in short it has also weight.

We must remember that Rutherford's model of the atom involves a central part or nucleus which is not a negative electron, nor an accretion of negative electrons, and in this part the principle or whole mass of the atom is supposed to reside. Because the opinions of some of the leading physicists concur in regarding the nuclear part of the atom as comprising one or more positive electrons according to the magnitude (atomic mass) of the atom, it by no means follows that its mass is electromagnetic in the same way as the negative electron exhibits this property, though we might conclude that it was from Thomson's 1881 calculation (see below). Moreover, it is not known whether this positive atomic electricity exists in the atom without being associated with or residing on a material part, such as a hydrogen atom (or a number of these) considered apart from the positive electricity as such. Furthermore, if I understand Silberstein aright, he is inclined to the view that the negative electron may have, besides electromagnetic mass, some ordinary mass, and I venture to suggest here that these states of matter (if this idea be allowed—see below) whereby they exhibit one or the other kinds of mass (or both together) may undergo variation, so that the electron in the atom may not have the same mass-properties as the free electron which has been expelled in radio-changes.*

Returning to the subject, Mr. Redgrove says:—"If we examine the various definitions of matter which have been put forward, we shall find that many of them are incapable of quantification, and the one which is most readily quantifiable—namely, 'matter is extended substance'—gives volume as the measure of quantity of matter. Indeed, to give Mr. Loring's definition of 'mass' any semblance of justification, 'matter' must be defined in a sense wholly divorced from common usage."

I take this to mean that the definition of mass given by me on p. 301 (1st column) would involve a volume measurement of matter. Surely "quantity" in the sense used is not necessarily "volume," nor is matter necessarily "extended substance." On the contrary, if we must have a definition of matter, it is something that has gathered itself together, starting with a formless continuum (3rd state of matter?), or vast mist-like "extension of substance" (transition state?), as suggested many years ago by Sir William Crookes. Then, if I may continue, the "transformation" I spoke of is the *time process* (see CHEMICAL NEWS, cxi., 157) whereby this extended substance has gathered itself together (passing into the 4th state?); even the atoms themselves are accretions of negative electrons *in part*; suppose that we cut short a long argument and simply say—the more this substance gathers itself together the more it tries to get together: hence the acceleration: hence gravity: hence (as a result) matter as we know it: hence mass. It is to be noted that the "states" of matter above designated are here employed in a fundamental sense, as distinguished from common usage.

Referring now to the term *weight*, I thought I had made it clear that weight is force, and that it varies with

* I have been working a long time on the idea of electrons travelling over their time distances, and thus becoming transformed, but this conception involves all kinds of difficulties; for instance, a 4th dimensional spiral time-course. See remarks below, following quotation from Lodge.

place, while it is a conjoint effect. Mass, however, remains unchangeable. Hence we can use the expressions—the conservation of mass, the centre of mass, the atomic mass.

We use the expressions—weight of one gramme, conservation of weight, and atomic weight. These are quite accurate statements when we take into account the idea that these expressions are synonyms for a constant force-value referred to, or taken at, a certain place; namely, in the case of the gramme weight a force of 981 dynes, involving Paris as the standard place of reference—very much as the boiling-points of bodies are referred to a certain atmospheric pressure, or accelerations of gravity are specified in, or reduced to, sea-level values. The actual weight would obviously vary slightly from place to place (just as the boiling point of a given substance would vary if taken at different atmospheric pressures), but this fortunately does not trouble us, since, in practice, we are able to duplicate the quantity of matter represented by the standard weight by means of a counterpoise balance; hence it is argued, justly, that it would be better to substitute the term *mass* for *weight*, and thus avoid the mental transference of a weight to a certain standard place when we “stop to think” what the *weight* really means. I agree with my critic that one superfluous term should be abolished, but I hold that the term *mass* should be retained and the term *weight* gradually eliminated in scientific writings when gravitational attraction is not under special consideration. We should then ordinarily say *atomic mass* rather than *atomic weight*.

Mr. Redgrove says that the expression “ratio of mass to weight” is not admissible. Sir J. J. Thomson uses this expression in his “Atomic Theory,” p. 18, where gravity comes into special consideration in reference to mass. Moreover, I do not see why a ratio should have a negative significance so as to debar it from association with other mathematical relationships, nor do I see why certain quantities of different kinds cannot stand in some simple relationship to each other when they belong to one equation. I do not know that Mr. Redgrove has all this in mind, but he says that it is not legitimate to compare mass with weight because they are not of the same kind. A good deal depends upon how the ratio is used, and no doubt Mr. Redgrove is right in the sense intended.

Mr. Redgrove’s “higher” criticism is worth careful study in my opinion, and I am quite aware that if we introduce the principle of relativity, for example, then the argument in defence of my statements shifts ground somewhat, since this principle is of universal application. Indeed, I have borrowed from H. G. Wells and Minkowski in respect to the time ideas, but notwithstanding, I submit that it is desirable to treat mechanical problems independently and in the orthodox manner.

By the way, those who wish to get an idea of this doctrine of relativity, which was primarily evolved to reconcile certain optical anomalies, should read the last two chapters in Prof. Wood’s “Physical Optics” (Macmillan, 1914). There is also a review of Dr. Silberstein’s “Theory of Relativity” in *Science Progress*, January, 1915, which is also helpful.

Referring again to electrical matters, in Sir Oliver Lodge’s “Electrons,” chap. II., a very interesting treatment of electrical inertia is given. I will quote a parallel drawn between electrical and mechanical relations:—“An accelerated charge is equivalent to a changing current, for dC/dt may be written d^2e/dt^2 . Whenever a current changes it is well known that an E.M.F. of self-induction is set up, equal to LdC/dt ; and this electrical equation $E = LdC/dt$ corresponds to the mechanical equation $F = m\ddot{x}$ —Newton’s second law.” We are not, however, justified in assuming that electrical mass or inertia is the same thing as mechanical mass or inertia. As already suggested, we may have different states of matter (third and fourth, for instance), consequently different kinds of mass (electrical and mechanical), and I think that we should not mix these up indiscriminately. In the *Philosophical*

Magazine (April, 1881) J. J. Thomson showed that a positively or negatively charged sphere in motion had a “quasi inertia,” due to the electrical charge. This remarkable effect has been verified in the β -particle experiment (see above).

Speaking of electrical inertia generally, as exemplified in alternating current work, I should like to point out that the phase displacement of current components, or the time-lag of E.M.F. relative to current, due to self-induction, can be very well illustrated by mounting two small massive wheels on shafts (in bearings) and joining their ends together by means of a short, stout, but soft rubber tube (wired on at each respective end); by turning one wheel to and fro through a small arc (by hand) it will be seen how the other wheel partakes of the same to-and-fro motion (simulating, though imperfectly, the alternating current), but a lag in movement takes place, illustrating the effect of self-induction. This being an inertia effect, it should be helpful to those unacquainted with electrical inertia, which resembles mechanical inertia. I need hardly state that I am not here addressing this remark to Mr. Redgrove, as he doubtless knows as much if not more about these matters than I do.

In conclusion, it may be of interest to note a passage from Dr. Owen’s book “Recent Physical Research,” p. 110 (The Electrician Publishing Co., 1913):—“Now a change in mass involves the breakdown of Newton’s second law of motion. It appears, then, that whilst in the case of the single negative electron this change does occur, no evidence of it is yet available in the case of matter, the atoms of which according to modern views contain electrons in numbers of the order of their atomic weights.” This is a concluding passage to a section on the “variability of mass.”

FURTHER NOTES ON THE REFRACTORY PROPERTIES OF ZIRCONIA.

By H. CONRAD MEYER,
Laboratory, Foote Mineral Co., Philadelphia, Pa.

THE remarkable heat-resisting properties of zirconia have been known for many years, but it is only within the last few months that serious attention has been given in America to its possibilities in metallurgy and furnace technology. The reader is referred to a previous article for a brief history and description of zirconia (*Met. and Chem. Eng.*, xii., 791, No. 12; *CHEMICAL NEWS*, cxiii., 30). Heretofore, zirconia has been considered one of the rare oxides, and hence of limited application. It is now being supplied, however, in commercial quantities, and in many instances is now being used on an industrial scale. A free exchange of ideas among many investigators has rapidly advanced the technology of zirconia, and the writer hopes that the preliminary data here given may be of value to all those now working on this new refractory body. Many of the investigations have been carried out by the author, and numerous independent reports have been secured from private sources, for which due credit is given.

Analysis of Natural Zirconia.

In the investigation of refractory substances a complete chemical analysis is often found of value. The presence of alkalis, silica, and iron oxide often plays an important part in the behaviour of the material when subjected to high temperatures. The mean of three analyses of an average sample of natural zirconia is given herewith:—

ZrO ₂	84.1
SiO ₂	7.74
Fe ₂ O ₃	3.10
TiO ₂	1.21
Al ₂ O ₃	0.66
Loss on ignition	2.72

It will be noted from the above that the only two oxides present which would be likely to cause a lowering of the melting-point of the zirconium oxide are silica and ferric oxide. The 1.21 per cent of titanium oxide present may or may not exert a fluxing action at high temperatures, but the practice seems to be, in manufacturing most fire-brick and refractory ware, to disregard this oxide entirely. The ignition loss consists mainly of moisture with a small percentage of organic matter.

Heat Tests on Zirconia.

(Data taken from the results of three or more tests on separate mixtures by G. T. Stowe.)

An ore containing 84 per cent ZrO_2 , ground to 100 mesh and mixed with H_2O , moulded easily into cones which kept their shape when burnt with little warpage or shrinkage to about the temperature of cone 35 ($1830^\circ C.$). These tests on cooling show a slightly vitrified material with a smooth and fine-grained surface.

Zirconia mixed with a 5 and 15 per cent mixture of Bens Creek clay, in view of finding a suitable bonding material, and heated to a temperature over cone 31 ($1750^\circ C.$), shows the 15 per cent tests to be in fair shape; that is, slightly vitrified, cracked, and coarser grained, while the 5 per cent test is in good shape with a fine finish, and very little shrinkage or warpage. A mixture of 5 and 15 per cent Warrior Ridge clay with the zirconia and heated to the temperature of about cone 32 ($1770^\circ C.$) shows the 5 per cent mixture to be in excellent shape with a clean cone standing at the end of the test. The 15 per cent mixture does not hold up quite as well at the same heat.

A mixture consisting of 98 per cent 100 mesh zirconia and 2 per cent slaked lime worked into a plastic form with H_2O , showed a fusion-point of about cone 30 ($1730^\circ C.$). Further, this cone lost its shape by warping at least five cones before the mixtures with clay.

The mixtures on a whole were easily moulded. The pure zirconia test cones seemed to have some plastic properties and held together very well, making a clean and sharp-edged cone.

The burnt product seems to be a likely refractory material, granting that the higher heat and flux standing properties make up for the advance in the cost of manufacturing the material in comparison with other refractory wares. The vitrified samples show a very hard and seemingly strong ware.

Of all the tests made, the 5 per cent mixture of Warrior Ridge clay with the zirconia seems to make the best bond; produces the best appearing samples before and after burning, the pure zirconia tests excepted, and those only as to heat tests.

Fire Shrinkage. (Author's Tests).

Small briquets of the following were carefully made measuring $36 \times 20 \times 5$ mm. These when thoroughly dried, were burnt at a temperature of approximately $1427^\circ C.$ in a No. 2 muffle furnace supplied by the American Gas Furnace Company.

No. 1. Pure zirconium oxide (99 per cent ZrO_2).

No. 2. Wet ground zirconia (84 per cent ZrO_2).

No. 3. Zirconia (95 per cent ZrO_2).

No. 4. 93 grms. of No. 3, and 7 grms. Dry Branch kaolin.

No. 5. 60 grms. zirconia, 80 mesh (84 per cent ZrO_2 , and 40 grms. wet ground zirconia.

Linear shrinkage at $2600^\circ F.$:—

No. 1	9 per cent
No. 2	9 "
No. 3	9 "
No. 4	12 "
No. 5	3 "

Briquet No. 1, made from pure zirconium oxide, analysing about 99 per cent ZrO_2 , yielded a sticky mass on mixing with water, and was quite soft after drying.

After burning No. 1 was still in a soft condition, and could be readily scratched with the nail.

Briquet No. 2 consisted of natural zirconia carrying about 84 per cent ZrO_2 , corresponding to the analysis given above. As indicated, this material was wet ground in a ball mill, and thus reduced to an extremely fine state of subdivision. It was readily moulded into shape. Firing rendered the material extremely dense and of a flint-like hardness. Several briquets were heated to redness, and one end plunged into a beaker of water. This quenching test apparently left the material unaffected, as no cracks were developed.

Briquet No. 3 was made from 95 per cent zirconium oxide. This 95 per cent product was prepared on a small scale from the natural or 84 per cent zirconia. Most of the silica and nearly all of the iron were removed by this refining, which yielded a light grey product. After firing, the briquets presented a very dense structure, and were extremely hard.

Briquet No. 4 shows the bad effect of even a small percentage of a very refractory china clay. Dry Branch kaolin is a pure white washed clay, having a fusing-point above $1790^\circ C.$

Briquet No. 5 was made from a mixture of 60 grms. coarse zirconia (material passing through an 80 mesh screen), and 40 grms. water-ground zirconia, or material similar to No. 2. It will be noted that the shrinkage in this case was extremely low. The briquet, after firing, presented a rather coarse porous texture, but possessed considerable tensile strength.

Whether these shrinkage figures would be greater at higher temperatures, it is difficult to say.

Selection of a Binder.

The proper choice of a binder is a very important consideration, as the fusing-point of the zirconia is influenced largely by the substance added as a bond. Phosphoric acid, sodium silicate, and lime were tried, but with indifferent success, and in many cases it was clearly apparent that such bonds were positively detrimental.

The following data were secured from a private source (R. C. Gosrow). The tests were made in the form of small briquets measuring $1\frac{1}{4} \times 1\frac{1}{4} \times 4$ in. in a steel mould. The material was rammed in place with considerable pressure. Five such tests were made as follows :—

1. Zirconia powder, bonded by $26.5^\circ B\acute{e}$. $MgCl_2$ solution (concentrated from salt bitter). Mixed to consistency of a stiff mud, and rammed. Dried five days— $100^\circ C.$ Dried eight hours— $150^\circ C.$ Heated gradually to bright red, and exposed to temperature of $1600^\circ C.$ in an electric arc furnace for two hours. The sample showed no fusion; corners sharp and hard, scratch glass, shrinkage slight, FeO and Fe adhere in molten condition, FeO showed corrosion, very dense, difficult to crack with bricklayer's hammer.

2. Zirconia powder, 50 per cent; dead-burnt magnesia (electrically dead-burnt), 50 per cent; bonded by $26.5^\circ B\acute{e}$. $MgCl_2$ solution, and mixed to hard stiff mud, and rammed. Dried same as 1. Heated to same temperature and for same time as 1. Fused to spongy mass, dark colour. The fusion was evidently caused by iron oxide and silica.

3. Zirconia powder 10 per cent; dead-burnt magnesia, 88 per cent; $26.5^\circ B\acute{e}$. $MgCl_2$ solution, 2 per cent. Mixed to stiff mud, and rammed. Dried and heated same as for 1. Hard dense compact brick, sharp hard corners, positively no fusion, showed no corrosion by FeO , light brown colour.

4. Zirconia powder, bonded by $30^\circ B\acute{e}$. Na_2SiO_3 solution to form stiff mud, and rammed. Dried and heated same as 1. No fusion, extremely hard, dense; interior appeared denser than exterior; slight crack in interior, probably due to moisture.

5. Zirconia powder, bonded by small amount of water in form of vapour, mixed to stiff mud, and rammed. Dried and heated same as for 1. Compares to properties of 1. Showed same FeO corrosion.

With the exception of 2, which fused, the samples showed:—

1. General corrosion by FeO in spots.
2. Slight shrinkage.
3. Withstood temperature changes from 500° C. to 1600° C., without any cracking or spalling.
4. No contortion or deformation at high temperature.
5. Precaution necessary in choosing suitable binder, and also care to be used in mixing with other refractory substances containing impurities as FeO, SiO₂, &c.
6. Zirconia can be used equally with magnesia, and with less cost for linings, &c.

The results secured by Mr. Gosrow under test No. 3 appeared promising enough to warrant further investigation along this line. Preliminary tests indicate that magnesium chloride would be objectionable on a commercial scale. Hence, another binder was sought and ultimately found in water-ground zirconia. It was further considered that the dead-burnt magnesia (electrically dead burnt) might be successfully replaced by ordinary calcined magnesite, such as is used for magnesite cement in flooring. This product carries about 93 per cent magnesium oxide, with a small percentage of carbon dioxide, calcium oxide, and silica.

The following formulæ were used (by J. R. Adams under author's supervision) in the making of several small briquets which were carefully dried and burnt at a temperature of approximately 1427° C. in a small muffle furnace:—

Formula 3A.

- 45 grms. zirconia (ground to pass through 80 mesh screen).
45 grms. magnesium oxide (calcined).
10 grms. water-ground zirconia.

The briquets after burning were of a brownish yellow cast, with a rather loose texture, but quite resistant to abrasion and of a fair tensile strength. The fire shrinkage at the above temperature was approximately 8 per cent linear measurement. One of the briquets at a white heat was dropped in a beaker of water, but no cracks were developed, and the material was apparently as solid as before quenching.

Formula 3B.

- 72 grms. zirconia (ground to pass through 80 mesh screen).
18 grms. magnesium oxide (calcined).
10 grms. water-ground zirconia.

Briquets made from this formula had very much the appearance of those produced by Formula 3A. The fire shrinkage was approximately the same. The specific gravity was, of course, higher, owing to the greater percentage of zirconia present. The results of these tests were considered rather encouraging, and further investigations are now under way. The strong objection to the use of the magnesium oxide, particularly the calcined product, is the fact that it has an extremely high shrinkage. This of course is not true of the costly electrically shrunk magnesium oxide, but the tendency would naturally be toward the use of the cheaper calcined oxide.

Fire Clay Bond.

As will be noted under fire shrinkage, briquet No. 4, mixed with a 10 per cent bond of refractory clay, showed extremely high shrinkage. It was decided, however, to manufacture a few standard-size fire bricks, using a 5 per cent bond of Warrior Ridge clay, as mentioned above. The zirconia was ground to pass through an 80 mesh screen, and thoroughly mixed in a dry pan with 5 per cent of the aforementioned clay. The mass was slightly moistened, and formed into bricks in the same manner as is pursued in the manufacture of silica or chrome bricks. After thoroughly drying, these bricks were burnt in a silica brick kiln, at an estimated temperature of at least 1649° C.

No figures were secured as to the fire shrinkage, but even this small percentage of clay caused the bricks to soften at a temperature well below the fusion-point of the natural zirconia. The standard bricks made from the material weighed on an average 11½ lbs. each.

To determine the behaviour of the material when in contact with carbon at high temperatures (the following data were contributed by an experienced investigator, who requests that his name be withheld), a brick was made a part of one side of the trough of a granular carbon resistance furnace, the rest of the trough being made of magnesite brick, all being backed up by fire brick. A pyrometer tube was put in so as to give the temperature of the surface of the brick, next the carbon resistor, and temperatures read with a Wanner pyrometer. In about one-half hour after starting, the temperature was 1800° C. $\pm 25^\circ$, and it was held between 1750° and 1850° C., averaging 1800° C. $\pm 25^\circ$ for one and a-half hours. The furnace was then torn apart. The zirconia brick was just nicely red on the back (2½ in. from the resistor), while the magnesite bricks were much redder. From this and from the temperature of the fire brick backing when felt from time to time, it is plain that zirconia has a considerably lower thermal conductivity than magnesite, and quite probably the lowest of any available material that will stand 1800° C.

The brick when put in place had a slight crack, and this increased a little on heating, but not very badly. Magnesite bricks on both sides of it were badly cracked. A slight shrinkage was noted on the hot face, and the surface of the zirconia brick was slightly pitted and spongy. The spongy layer was only about ¼ in. thick. The magnesite bricks were considerably more acted upon by the carbon than the zirconia bricks, their surfaces being eaten away uniformly over ¼ in. Hence as regards the action of carbon on the hot brick, the zirconia brick appears superior to magnesite, but inferior to carborundum.

The zirconia brick was not supporting any weight, and only the inner face reached 1800° C. The brick had not really fused nor flowed of its own weight; i.e., it might not have failed under a "cone test" at 1800° C. Yet when the brick was picked up with tongs, they sank into the hot face, under gentle pressure, to a depth of ½ in.

The face of the brick was very plastic, and though it had not really fused nor flowed out of shape, the fact that the brick as a whole kept its shape was due to the stiffening effect of the comparatively cold back of the brick. If the whole brick had reached 1800° C. and had been under any pressure, as in a wall with other courses of bricks resting on it, it would certainly have been pressed out of shape.

It therefore appears that 1800° C. is the upper limit at which this brick (zirconia bonded by Warrior Ridge clay) could be safely used. It is, of course, quite possible that a brick bonded with water-ground zirconia and free from clay bond, might be stiffer and stand up at a higher temperature.

Therefore, while this particular brick is not as refractory under furnace conditions as the reported melting-point of zirconia would lead one to expect, it is still refractory enough to be classed among the half dozen highest refractories; while not entirely free from shrinking and cracking, its behaviour in this respect is far better than magnesite, although not as good as carborundum. Its heat conductivity is apparently less than any other of our high refractories. Its behaviour in contact with carbon, while not perfect, is not so bad but that it can probably be controlled.

Zirconia Crucibles and Similar Shapes.

In the manufacture of crucibles, muffles, &c., from zirconia, it should always be borne in mind that the material has an extremely low thermal conductivity. Hence, the walls of the crucible or other shape must be considerably thinner than would be the case if clay were used. Owing to the high tensile strength of zirconia when

properly bonded and burnt at a sufficiently high temperature, it is possible to make such objects without the danger of breakage through handling. Another important consideration in the use of zirconia in crucibles is its resistance to fluxes and slags. It has been suggested that water-ground zirconia might prove very efficient as a lining for graphite crucibles. Shallow dishes, trays, and small crucibles have been made experimentally by hydraulically pressing various mixtures of coarse zirconia bonded with water-ground material, producing ware of high tensile strength and of extreme thinness. Shallow dishes have been pressed in this way, having a diameter of 6 in. and maximum thickness of not over $\frac{1}{8}$ in.

Although this article does not concern itself with the uses and applications of chemically pure oxide of zirconium, it is interesting to note that two patents have recently been granted for the manufacture of utensils and the like from the oxides of the rare earths, such as thorium, zirconium, &c.

While the foregoing results should not be accepted as final or conclusive, they apparently presage important industrial uses for this new refractory.—*Metallurgical and Chemical Engineering*, xiii., No. 4.

EDUCATION FOR RESEARCH.*

By W. H. WALKER.

(Concluded from p. 24).

As a transition paragraph from the employer to the employee, I shall again emphasise the point already treated elsewhere. For the best results a manufacturer should realise that his organisation must teach the college man the details of the work for which he is employed, and the new graduate must realise that there is an enormous lot which he does not yet know and which the factory superintendent or foreman can best teach him. Fault is frequently found with the college man because he does not know the latest quick analytical methods as used in some large laboratory—that he is not familiar with the types of machines employed in the factory to which he goes. Inasmuch as the average candidate has but four years for his technical training, it follows that if he had been taught these details upon which his immediate success may possibly depend it would have been at the expense of a broad, fundamental training in economics and science, upon which his final success is sure to depend. On the other hand, there is much truth in the oft-repeated assertion that the college graduate "thinks he knows it all." He fails to realise that in every industry there is a great field of knowledge of which he is as yet ignorant, but which is familiar to the manager, superintendent, or foreman. Not only the details of factory procedure, but matters of finance, salesmanship, advertising, and other factors essential to the success of the undertaking are unknown to him.

Finally we come to the education of the man who is to do the research work. At this time it would be out of place to discuss curriculums of study or to outline courses of instruction, but there are two or three points which it may be worth while to consider.

In general it may be said that a man should possess the ability to utilise the knowledge he has acquired in the past in the solution of his present problems. This statement presupposes two things—first, the acquisition of knowledge, and second, a training in the application or use of this knowledge. Comparatively speaking the first is easy and the second is difficult. In a limited sense knowledge can be bought in the form of books, but no one

can appropriate to himself a skilled hand or an observant eye or an accurate analytical mind. These are the products of training. There is a regrettable tendency in modern text-books on elementary chemistry and qualitative analysis to spend an undue amount of time upon the laws of dilute solutions to the exclusion of that training which these subjects are pre-eminently fitted to give. Not that these laws are of little importance, but fundamental principles and broad generalisations are of value only when they can be visualised in terms of facts and experiences, but the present tendency to over-emphasise theory in elementary chemistry and qualitative analysis crowds out that knowledge of facts and training in observation in which the beginner is so deficient. The great difficulty with the average student in experimental science is that he sees things as he thinks they ought to be and not as they are. He does not observe accurately nor reason logically. He is not resourceful in using the knowledge acquired yesterday in solving the problems of to-day. Such power can be obtained only by practice, and why postpone the practice of this all-important function until late in the college course? From my experience as a teacher, it is my opinion that no subject in the entire curriculum is so well adapted to train a man in keen observation, logical deduction, and general resourcefulness as a broad and sympathetic course in qualitative analysis. The short time usually devoted to this subject should not be consumed in teaching advanced theory, which can be better learned later.

A second factor in the education of a research man (but which of course is not limited to a research man) is the necessity of giving him a working knowledge of the general principles of chemistry, in the same manner that a mechanical engineer is made familiar with those principles of physics involved in thermodynamics and applied mechanics. So I use the word *working* advisedly, and mean thereby not only a knowledge of the fundamental theories and laws involved in every-day phenomena, but an acquaintance with them intimate enough to enable him to make daily use of them. The average student knows well the law of conservation of energy and of mass; although his arithmetic is usually poor the law of multiple proportions is second nature to him, and he handles it with ease. This is because the law is valid at all workable concentrations, at all workable pressures, and at all workable temperatures, and he has met with problems for the solution of which its application is imperative. Not so with the laws which he meets later in his work. In his course in Theoretical Chemistry, or Physical Chemistry, or General Principles of Science, or whatever name it may be called, he learns, for example, the law of mass action; if he solves any problems at all they involve dilute solutions or low pressures alone. He learns that for concentrated solutions and strongly dissociated salts the law does not hold, and there the matter rests. He learns Henry's law, Raoult's law, the law of electrolytic conductance, transference, osmotic pressure, &c., and if the subject is well presented solves numerical problems to render clear his mental image of these laws; then he learns that under those conditions in which he lives and moves and has his being they do not quantitatively hold, and there matter rests.

Imparting to the student a knowledge of these general laws of science is one of the most important factors in technical education, and must play a leading part in the upper year of college work, but the point I would emphasise is that when these principles are presented the task is only begun. The first instruction must of necessity be given, set as it were in dilute solutions. To be of pedagogic value the work must be quantitative, and accuracy can be realised only in very low concentrations. But here is where the average teacher of so-called theoretical chemistry "lies down on the job." To have a working knowledge of these principles a man must be familiar with their use under the conditions of concentration, temperature, and pressure with which he has to deal. He must

* Address at the Joint Meeting of the New York Sections of the American Chemical Society, the Society of Chemical Industry, and the American Electrochemical Society, Chemists' Club, December 11, 1914. From the *Journal of Industrial and Engineering Chemistry*, 1915, vii., No. 1.

have a general idea of the deviation from the theoretical which a law will suffer under working conditions. If such laws are not quantitatively applicable they are at least qualitatively helpful; if they do not determine how far one can go to reach a definite end they at least indicate the direction he must go. Our experience with men who have had a course in the general principles of chemistry is that they do one of two things—either they attempt to use the knowledge thus obtained and develop a confidence in their ability to get at the roots of the problem, and by applying these general principles determine the lines along which success most probably lies, or, to use an analogy, they are afraid to venture into the open ocean of practical experience with a boat which they have sailed only in the closed and secluded harbour of dilute solutions. The result is that they lose interest in the boat and soon entirely forget her. Had they been taught to navigate this boat in times of storm and high tides as well as in the harbour they might not have attained on the ocean the accurate time they were accustomed to make in the harbour, but they would the more quickly have reached the haven of success which lies on the opposite coast.

It is but a truism to say that the way to acquire an ability to solve problems is in the exercise of this faculty. To become a successful research worker we must do research work. While in every institution an attempt is made to train students to carry on original work, the four years allotted to the average man are not sufficient for accomplishing very much in this direction. While a genius is born not made, good experimentalists can be produced from most men of average ability.

It is believed that the training to be obtained from investigation work is largely independent of the particular type of problem undertaken. If one wishes to become a bridge builder by the experience of building bridges, it is not material whether the bridge so built is demanded by the travelling public or not. It is in solving the problems incident to construction, not in the use of the finished structure, that the educational value lies. Thus it is with research work in so-called pure and applied science—whether the results obtained be immediately used or very remotely used need not influence the methods employed in the work.

So in research laboratories bridges are built not only where the public is anxious to have them built but where some one is willing to pay for the building. The problems undertaken are brought by manufacturing concerns, and the expenses of the laboratories are met in this way. A twofold purpose is thus accomplished—the manufacturing public is given facilities for overcoming some of its difficulties, and the more able men of the community are trained to fill the demand, which is constantly growing and now far outmeasures the supply, for men capable of conducting successful original research.

A RAPID METHOD FOR DETERMINATION OF ESSENTIAL OILS IN ALCOHOL.

By W. B. D. PENNIMAN and W. W. RANDALL.

As the result of series of experiments carried out in the laboratory of the State Health Department, Baltimore, at intervals during several years, a method has been devised for the assay of spirits of camphor and of peppermint, and of the extracts of lemon, orange, peppermint, anise, and nutmeg, which appears to be more rapid and much more accurate than any method with which we are familiar. The facts which form the basis of the method may be grouped under three heads as follows:—

1. Camphor and the several oils enumerated above are completely expelled from solution in alcohol, when these solutions are mixed with from 4 to 10 volumes of a strong solution of calcium chloride.

2. The separated camphor or oil dissolves with the greatest ease in low boiling gasoline, an operation with

which alcohol, at least in the presence of such a calcium chloride solution, does not interfere.

3. Within certain fairly wide limits, the volume of the gasoline solution formed is exactly equal to the sum of the volumes of the gasoline itself, and the solid camphor (or oil) which has been dissolved.

The method here described is by no means entirely new. Schmatolla noted that when camphor dissolves in light petroleum oil, the volume relation stated in "3" obtains (*Apoth. Zeit.*, xvi., 290; *Abstr. Chem. Centr.*, 1901, i., [20], 1117; *Journ. Soc. Chem. Ind.*, 1901, xx., 756; Allen's "Commercial Organic Analysis," new ed., iv., 200). He employed a burette graduated in tenths cc. as a measuring apparatus, and weighed out the camphor spirit, which was later precipitated by means of saturated sodium chloride solution. We have secured better results by the use of calcium chloride solution, and prefer graduated milk-bottles and the use of the centrifuge as means of accurate measurement of small quantities. Arnost used a somewhat similar method to determine camphor in celluloid, correcting for alcohol dissolved (*Z. Unter. Nahr. u. Genussm.*, 1906, xii., 532; *Abstr. Journ. Soc. Chem. Ind.*, xxv., 1169). Chittick (*Proc. Assn. Am. Dairy, Food, and Drug Off.*, 1913, p. 160; *Chem. Abstr.*, 1914, viii., 1847), we have found since these experiments were made, used a method similar to ours for peppermint, precipitating the oil with water, and, by means of a blank, correcting for alcohol dissolved. We have not found water a satisfactory precipitant, and believe that much time can be saved without decrease in accuracy by the use of pipettes and the avoidance of weighings.

The apparatus called for consists simply of several accurate full pipettes, a Babcock centrifuge, and one or more accurately graduated Babcock milk-bottles. If the divisions on the neck of the bottle be from 0 to 10, then the graduated portion will contain just 2 cc. With a magnifying glass the volume of a column of supernatant solution in the neck of the bottle can be read with accuracy, probably to 0.008, perhaps to 0.004 cc.

As the volume of gasoline used should not be much less than, nor much more than twice as great as that of the camphor or oil to be dissolved (if the volume-relation mentioned under "3" is to hold good), it is well to work with such quantities that not much over 0.5 cc. of camphor or oil is to be determined. Thus we have found that 5 cc. of the alcohol solution serves well for strengths from 5 to 15 per cent; 10 cc. is probably better for 4 per cent solutions or anything weaker. The quantity of gasoline should, in general, be somewhat greater than that of the oil.—*Chemical Engineer*, xxi., No. 3.

New Volumetric Process for Determining Nickel.—Gino Zuccari.—Nickel can be determined volumetrically by the reaction represented by the equation $\text{Na}_2\text{Fe}(\text{CN})_5(\text{NO}) + \text{NiSO}_4 = \text{NiFe}(\text{CN})_5\text{NO} + \text{Na}_2\text{SO}_4$. A solution of sodium nitroprussiate is made by dissolving 74.482 grms. of salt in a litre, and it is allowed to drop slowly from a graduated burette into the nickel solution which is meanwhile stirred with a glass rod. When the precipitate of $\text{NiFe}(\text{CN})_5\text{NO}$ appears pale ash-coloured a drop of the liquid is filtered off and tested with Na_2S . A black stain of NiS is formed if the nickel is not completely precipitated. When the reaction is finished a transitory violet coloration is obtained. By multiplying the number of cc. of sodium solution used by 0.01467 the number of grms. of nickel in the solution under examination is obtained. This method gives good results if certain precautions are observed. The nickel solutions used must have concentrations not lower than 1 to 1.5 per cent. During the titration the liquid must be well shaken, specially towards the end of the reaction, in order to facilitate the precipitation of the nickel. Fine and non-porous filter-paper must be used, and it is best to carry out the titration in acid solution. The volumetric nitroprussiate method does not give good results with cobalt.

PROCEEDINGS OF SOCIETIES.

SOCIETY OF CHEMICAL INDUSTRY.

ANNUAL GENERAL MEETING, MANCHESTER,
Wednesday, July 14, 1915.

PRESIDENTIAL ADDRESS BY PROF. G. G. HENDERSON.

THROUGHOUT the period which has elapsed since the date of our last Annual Meeting the Society has had to carry on its work under conditions without parallel in its previous history, and unhappily still prevailing. Many of the members are on active service with the forces of the Crown, and some, we note with sorrow, have already fallen in the defence of our country; many others are strenuously engaged in no less important and honourable national service at home. The terrible but inevitable conflict which is being waged between civilisation and Teutonic barbarism so completely absorbs the thoughts and energies of most of us that other matters appear by comparison trivial and of little account. In circumstances such as these it is a reason for congratulation and a testimony to the inherent strength of the Society that little or no falling-off in its activities can be observed. The local sections have held their customary meetings and have contributed at least an average number of papers for publication. The *Journal* has appeared as usual, and although there has been an unavoidable interruption in the supply of those foreign periodicals from the contents of which a number of the abstracts are prepared, yet the energetic work of the editorial staff and the Publication Committee has to a large extent made good the deficiency; indeed, I think it will be generally agreed that there has been an improvement rather than otherwise in the quality of our publication. Finally, we are now assembled in General Meeting, as in every year since the Society came into existence.

From time to time during the year the sad duty has been imposed upon us of recording the death of one of our members. The customary obituary notices have been published in the *Journal* in due course, but I feel that it would not be fitting to pass over without further mention the loss of three of the original members of the Society who can ill be spared—Eustace Carey, Russell Forbes Carpenter, and David Alexander Louis. Mr. Louis was for long one of the staff of abstractors and a valued member of the Publication Committee, on which his untiring efforts to maintain the high standard of the *Journal* were of the greatest benefit. Mr. Forbes Carpenter's services to chemical industry in the capacity of Chief Inspector of Alkali Works can hardly be over-estimated, and his services to the Society were no less valuable. Mr. Carey was one of the small band of enthusiastic and far-seeing men who laid the foundation-stone of the Society. He devoted himself to its interests in almost every possible office—as member of the first Publication Committee, as Honorary Northern Secretary, as Chairman of the Liverpool Section, as Member of Council, as Vice-President, and in 1906-1907 as President. So recently as last year he attended the general meeting at Nottingham, and he was again a Member of Council at the time of his death. The Society has indeed suffered a heavy loss, but the memory of these upright and lovable men will long remain an incentive to continued progress.

The Society, in common with other scientific societies and institutions, has been eager to render every possible assistance to the Government in carrying the war to the successful issue which we confidently anticipate, and has had the satisfaction of supplying useful information to several Government departments on a number of occasions. I confess to disappointment, however, that fuller opportunities of national service have not been afforded. Many individual members of this Society, and of all the other scientific societies, have been and are doing splendid

work, but it is safe to say that better results would have been achieved by *organised* effort, and it is regrettable on all grounds that the scientific resources of the nation have not been systematically utilised by the Government as they might have been. Organisation has been lacking, with the result that comparatively little advantage has been taken of those resources, and yet it would surely not be a very difficult matter to bring into close co-operation all the societies representative of the different branches of pure and applied science. It would only be necessary to appoint some central body, which should have the duty on the one hand of keeping in intimate touch with the Admiralty, the War Office, and the Ministry for Munitions, and on the other hand of referring to the Council of each society the questions with which it is particularly fitted to deal. Whatever method be adopted, it is not by any means too late to set about the organisation of the powers which science can place in the hands of the Government, and the sooner this is done the better for the country. In this connection it is gratifying to note that a Committee, on which the Society is well represented, was appointed last August by the President of the Board of Trade to consider and advise as to the best means of obtaining for the use of British industry sufficient supplies of chemical products, colours, and dyestuffs of kinds hitherto largely imported from abroad. The problem how best to utilise the opportunities afforded by the war for extending and developing the chemical industries of the country has been discussed at meetings of a number of the local sections, and much information bearing on the question has been made available through the medium of the *Journal*. Whether as a result of this or not, even the most pessimistic must admit that British chemical manufacturers have already given evidence of their readiness to extend their operations and to undertake the preparation of many chemicals of different kinds which up till the present time could only be obtained from foreign sources, and that such indispensable materials as filter-paper and glass and porcelain ware for chemical purposes are now being successfully manufactured in this country.

In the report submitted by the Council to the General Meeting last year it was intimated that a Committee had been appointed to consider the best methods of increasing the usefulness, and incidentally the membership of the Society. After much careful inquiry the Committee presented a report, which was considered at a special meeting of the Council and generally approved. The main conclusion arrived at was that in the first instance no more important step could be taken than to endeavour to make the *Journal* as comprehensive, as informative, and, last but not least, as interesting as possible. An advance towards this end has been made in adopting a clearer and more legible type, in extending the scope of the published matter, and in issuing reviews and not merely notices of new technical books. Further developments will be carried out as circumstances permit, amongst others the publication at suitable intervals of reviews of progress and recent developments in the different branches of chemical industry, and it is hoped that the result will be to render the *Journal* simply indispensable to every chemist, if indeed that is not already the case.

Among the proposals for widening the sphere of influence of the Society submitted to the Council was one for the establishment, under the auspices of the Society, of an Information Bureau, which should have the duty of collecting, classifying, and distributing information of every kind likely to be of advantage to British chemical manufacturers. Obviously it would be foolhardy to engage in such an enterprise without full inquiry and careful calculation of the cost, and sufficient data are not yet at hand to justify the Council in coming to a decision. However, a committee has been appointed to gather information and to work out details, and although it is too soon to say what the outcome will be, I hope that the difficulties which stand in the way will be overcome, and that my successor in the presidential chair will have the satisfac-

tion of witnessing the inauguration of the scheme during his term of office.

Still another weighty matter which has engaged the attention of the Council is the character of the Annual General Meeting. I have for long held the opinion—in common, I believe, with many of the members—that full advantage has not been taken in the past of the opportunities afforded by the gathering together at the Annual Meeting of technologists representing most if not all of the branches of chemical industry, and that too much of the time over which the meeting extends has been devoted to purely social functions. Consequently it gave me great satisfaction when the Council came to the decision that at future General Meetings, whilst the social aspect will not be by any means neglected, the greater part of the available time will be set apart for the discussion of subjects of general interest to the members and for visits to works. We hope that the Annual Meetings of the Society will henceforth be looked forward to by all the members as congresses of technologists for the consideration of manufacturing problems and for the interchange of information and ideas, and yet none the less as occasions for the renewal of old friendships and the formation of new ones. With the cordial co-operation of the Manchester Section, to whose Chairman the special acknowledgments of the Council are due, the programme of the present meeting has been arranged on these lines, and that programme speaks for itself.

In order to encourage the entrance of the younger members of our profession to the Society, the Council have decided to entertain for a time applications for election without payment of the entrance fee from candidates whose position requires this special consideration. It is hoped that this concession will result in the addition to our ranks of a number of the younger chemists, and that thereby the desire of the Council to enrol every chemist in the Empire on our list of members will be brought nearer realisation.

It must not be forgotten that in considering the proposals for increasing the activities of the Society which have been laid before them the Council have had to bear in mind the effect on our financial position which might follow from the adoption of these proposals. The expenditure of a society such as this tends naturally to grow, and indeed increased outlays are inevitable if the standard of the *Journal* is to be maintained, or if, as some of us hope, it is to be raised to a still higher level. On the other hand, a corresponding increase of income cannot be counted upon, and in fact during the past year we have had to face a not inconsiderable falling-off. Consequently, whilst we are at one in the conviction that our watchword must be progress, and that we must not hesitate to break out new trails for the reason that the old one has led to creditable success, yet the Council, as trustees for the members, are morally bound to safeguard the resources of the Society and to very carefully weigh the consequences before embarking on any new scheme which involves inroads on the funds.

An encouraging illustration of the Society's vitality is the recent foundation of a new local section. A strongly supported request from chemists in Edinburgh and the East of Scotland for sanction to carry out this project was willingly agreed to by the Council, and I had the pleasure of presiding at the formal inaugural meeting on April 14, when Prof. James Walker was elected Chairman and a representative committee appointed. The new section starts under the best auspices, and there can be little doubt that its existence will be of benefit both to the industries of the district and to the Society.

Perhaps the most notable events of the year were the resignation of Mr. Watson Smith from the post of editor of the Society's *Journal*, which took effect on December 31, and the appointment of his successor. The General Purposes Committee, to whom was committed the task of considering the numerous applications for the vacant post, were unanimous in recommending that Mr.

T. F. Burton should be appointed, and, as you are aware, this recommendation was adopted by the Council. The new editor had not to take up duties which were altogether strange, because for a number of years previously he had done excellent work in the capacity of Assistant to the Editor and to the General Secretary, and a glance at the numbers of the *Journal* which have appeared since the beginning of this year will, I am convinced, lead to the conclusion that he is well qualified for the important position which he now occupies, and that in selecting him the Council chose wisely. I sincerely hope that he will have as long and as highly creditable a period of office as his esteemed predecessor, of whose services to the Society it is difficult to speak too highly. In his Presidential Address to the first Annual Meeting of the Society, held in July, 1882, Sir Henry Roscoe used the following words:—"The Publication Committee appointed by the Council to carry out and superintend the issue of a journal was fortunate in securing the services of Mr. Watson Smith, of the Owens College, as editor." It is only necessary to examine the long series of volumes which appeared under his care in order to realise that the Society was indeed fortunate in the appointment of its first editor. The editorship in Mr. Watson Smith's hands, extending as it did over a period of thirty-three years, not only became the work of his life, but was to him in truth a labour of love, and the members cannot permit him to retire without expressing, as I now do on their behalf, their deep appreciation of his long-continued, untiring, and devoted service. It is gratifying to know that the Publication Committee will continue to have the benefit of his wide knowledge and ripe experience.

The resignation of the first editor naturally carries one's thoughts back to the days when the *Journal* came into existence under his charge. The early history of the Society has been recorded in most interesting fashion in the addresses of two former Presidents, Sir Edward Thorpe and the late Dr. Divers, which almost completely exhaust the subject. However, through the courtesy of Mr. Watson Smith I am enabled to add some reminiscences of the movement which led to the foundation of the Society. These are contained in the following letter, written to him in 1895 by the late Mr. George E. Davis, who at the inception of the Society held the post of Honorary General Secretary:—

"In 1875 the Faraday Club was formed; in fact it was got together by myself, on account of the chemists of Widnes and St. Helens scarcely knowing each other. Some of the chemists when approached on the subject would not join, as they said that a similar attempt had been made some five or six years before to form a chemical society in St. Helens, and the masters had prohibited their chemists from attending the meetings. In fact the feeling was so great even at the formation of the club that some few weeks after the first meeting Mr. Gamble came into my laboratory and told me he had heard I was connected with a secret society, and desired to know whether this was the case or not. I told him that whether it was called a secret society or not, it was a combination of chemists having no interest but their own profession, and had no adversaries so far as they were concerned, and that he might safely trust me, being the secretary, to do what was right. He left me quite satisfied, and the club went on, we holding our meetings every fortnight, and alternately in Widnes and St. Helens. By and by the club became more interesting and was moved to Liverpool, where we used to meet at an hotel which is now pulled down owing to the station improvements. The club thus continued until 1879, and has never been dissolved. In 1879 some members who had refused to join us at the start wanted to come in, and as they were not allowed they endeavoured to form a society of their own in Widnes. I believe a meeting was called in the Drill Hall, Widnes, with Mr. J. L. Muspratt in the chair. The meeting appointed a committee to draw up rules, of which I myself, Dr. Hüter, and Douglas Herman were

members. These rules were printed, and the committee met several times to discuss them, but they were not to my liking, and I was afraid the Faraday Club would suffer by the division. Several meetings were held, and at last it was suggested that the society should be called 'The South Lancashire Chemical Society,' when I pointed out that it would be folly to call the Society 'The South Lancashire Chemical Society' when Manchester was included in it, and we had not asked Prof. Roscoe, the head of the Owens College Laboratories, to take the leading part in it. Meetings were then held in Liverpool, and Mr. Mond became interested, he, I believe, taking the chair at one of the meetings there. After seeing Prof. Roscoe a meeting was called for Owens College, and about four-and twenty members, representative of the chemical and allied interests, sat round the table there. It was proposed to found a society to be called the 'Society of Chemical Engineers.' Up to this time Mr. John Hargreaves had been secretary of the movement, but he became frightened at the immense amount of work the scheme would require, and asked me if I would take the secretaryship if he gave it up, as, he said to me, 'they are making the society a national one, and the next move will be to make it international.' I said, 'And why not? The bigger the scheme is the more honour will be attached to it.' I took the Secretaryship from that point, and the next thing was to call a meeting for London. I am not quite sure where that meeting was held, but I rather think it was in George Street, Westminster, and the idea which ran through the minds of all concerned was the formation of a society to represent chemical engineering. We all went up to that inaugural meeting with the idea of carrying out this scheme, but when the meeting was held one or two of the professorial type foresaw that if it was a Society of Chemical Engineers it was more than probable they would be left out in the cold. The position was rather serious, and as I sat by the side of Prof. Roscoe as Secretary the thought struck me that if we could give the Society a kind of indefinite title it would stifle all opposition and would go through. I therefore wrote a resolution that the Society should be called 'The Society of Chemical Industry,' and gave it to Weldon to propose. Our proposition was carried, and the way was smoothed over by allowing anybody who signed the requisition form before a certain date to become members of the Society without election, and I believe some three or four hundred availed themselves of this.

"Now with regard to the *Journal*. The idea which ran through my mind was a journal precisely as we have it now, the size of the *Athenaeum*. I think we had a meeting at the Café Royal to decide whether a journal should be published or not. I had in my own mind come to the conclusion that without a journal such a Society as this would be a barren one and would not last long. Most of the members of the committee objected to a journal being started, and said that we could never find matter enough to fill it, and this they repeated during several meetings. When we held our first General Meeting papers were read at it, and although I suggested the *Athenaeum* form for printing the proceedings I was out-voted, and our first *Proceedings* were printed to imitate as nearly as possible, but with a blue cover, the *Proceedings of the Chemical Society*. How far my judgment was correct is proved by the reprinting of that volume of *Proceedings* into the present *Journal* size. When I proposed that the *Journal* should be large enough to take large illustrations I was laughed at, and it was said that children looked over the pictures but not scientific men. Well, the *Journal* would never have been started, in my opinion, had it not been for Mr. Mond. He clearly saw the necessity for such a journal, and a guarantee fund was formed at his suggestion, and he headed the list with a promise of a hundred pounds. It is a matter of history that not one penny piece of that guarantee fund was ever touched. From this first number I believe you know all

the rest, and your labours in connection with that *Journal* have served to make it the leading journal of chemical industry and the bond which has held together all the sections of the Society.

"With regard to the sections, I had the utmost difficulty in getting the London Committee to see the necessity for their formation, but I carried my point. I have never regretted the strong measures and the strong arguments which I used in those days."

Mr. Davis's recollection of the incidents associated with the formation of the Society may have been at fault here and there, but, even if this is the case, it appears to me that his racy and intimate narrative is well worth preservation. The rest of the story of the foundation may be told in a few sentences. Following on the preliminary meetings mentioned by Mr. Davis, in October, 1880, a circular letter was issued by Prof. Roscoe, who had acted as Chairman of the Provisional Committee appointed to promote the scheme, in which notice was given of the proposal to establish a society to be called "The Institute of Chemical Engineers or the Institute of Chemical Industry," and the support of leading members of the chemical industries solicited. The response to this letter was so encouraging that the Society was formally brought into existence early in 1881, Prof. Roscoe being elected President and Mr. George E. Davis Hon. General Secretary. In the Report of the Council presented to the first General Meeting of the Society, which was held in London on June 28 and 29, 1881, the future policy of the Society was outlined in the statements that "Annual General Meetings will be held in various towns throughout the country," and that the Council had "arranged for the establishment of local sections," and "had under consideration the propriety of publishing a journal." It is evident that the Council did not long delay in coming to a decision on the last point, for in October of that year Dr. Mond, after consultation with Dr. Angus Smith, proposed to Mr. Watson Smith that he should become editor of the projected *Journal*. The first number appeared in January, 1882, and the history of the Society's growth and development is written in the succeeding volumes.

Since the outbreak of the war there has been much discussion concerning the present position and the future prospects of the chemical industries of this country, and I earnestly hope that the serious consideration which has been given to the subject will have at least one result—that we shall refrain from talk and proceed to action. We have been made to realise more clearly than ever before that during the last forty years chemical industry in Germany has made marvellous strides in advance, whilst in this country it has by comparison stood still, or even gone back. We have to admit that certain branches of applied chemistry, particularly the manufacture of dyestuffs, of synthetic drugs, and of organic compounds and fine chemicals in general, have passed almost wholly out of our hands, or rather have never been taken up to any notable extent in this country. We cannot deny that the Germans have with energy and success developed on the industrial scale many scientific discoveries, such, for instance, as the various methods for the fixation of atmospheric nitrogen, whilst we have done little or nothing in that direction. Even our former supremacy in the manufacture of heavy chemicals has been seriously attacked. These are the facts, and whilst there may be differences of opinion as to the principal causes of this unfortunate state of affairs, yet I think that no unprejudiced person, who is prepared to study the question dispassionately, can have much doubt in his own mind as to the real reasons for German progress and British backwardness. The position has already been stated so often and in such a clear and comprehensive manner by a number of leading chemists—and in this connection I desire to draw your special attention to the Presidential Addresses delivered recently by Professor Meldola and Professor Perkin to the Institute of Chemistry and the Chemical Society respectively—that I may well be excused from

repeating the arguments which, it is to be hoped, are at long last beginning to make some impression. There is, however, one aspect of the question on which I may venture to add a little to what has already been said. It appears to me that the time has come when we may profitably desist from arguing about the causes which have hindered a development of our chemical industries such as has been witnessed in Germany. Let us admit frankly that we have left undone many things which we ought to have done, and having confessed our sins let us unite in striving to secure the future prosperity of our industries. Now, in my judgment, the two main causes of our lack of progress are as follows. Firstly, we have failed to realise that "scientific research work, carried out in the laboratory, is the soul of industrial prosperity"—that modern chemical industry must of necessity be based upon research if it is to meet with success. This axiom may indeed have been tacitly accepted, but, speaking generally, it has not to a sufficient extent been made a guiding principle in our chemical industries. In the second place, there has not been in the past a sufficiently close and intimate interchange of information and opinions between manufacturers and professors of chemistry; in fact, most unfortunately for both manufacturer and teacher, the attitude has rather been one of mutual aloofness and reserve. If this is an accurate statement of the position, as I believe it is, it follows that we ought to seek means of rectifying these errors.

A welcome move in the right direction on the part of the Government was intimated in the House of Commons on May 13th by the President of the Board of Education, who stated that he was including in the estimates a sum of £25,000 to £30,000 for the purpose of instituting an Advisory Council on industrial research which should represent the various industries of the country and work in co-operation with the Board of Trade to secure closer association of science and industry. This action is bound to be productive of good, if sufficient funds are available, but Government assistance, much as it is required, will not by itself bring about the desired result; all interested in chemistry must also take an active part. Consider for a moment the present state of affairs. It is in many cases difficult if not impossible for chemical manufacturers to carry out the systematic research work without which their business must sooner or later decline, either because they have not the necessary staff of properly trained chemists, or else because their chemists, although qualified to prosecute the experimental investigation of technical problems, are fully occupied in analytical work or in the supervision of manufacturing operations. This difficulty is perhaps most prevalent in those industries which are not usually classed as chemical in spite of the fact that they are based on purely chemical processes. On the other hand, in the Universities and Technical Colleges there is a considerable number of graduates engaged in research, and this number could be greatly increased if more inducements were offered and facilities provided for students who are both able and willing to undertake such work but who for lack of means are compelled to seek a salaried post as soon as they have completed the minimum cost of training. Very little of the research work done in our chemical schools has any direct bearing on chemical manufactures, and yet, from the educational point of view, there is no reason why some at least of this army of young research chemists should not be engaged in the attempt to solve problems in applied, instead of in pure, chemistry. Obvious difficulties in carrying out such a suggestion at once present themselves, but many if not most of these could be set aside by the institution of schemes of Industrial Fellowships, more or less on the lines of that successfully inaugurated by the late Prof. Kennedy Duncan in connection with the Universities of Kansas and Pittsburgh. The essence of this eminently practical idea is that any manufacturer who desires to have some technical matter investigated applies to the chemistry department of a University or Technical College for the

services of a chemist qualified to prosecute research, and undertakes to provide adequate remuneration for a period of one or more years; the work is done in the chemistry department under the general superintendence of the Professor, and, if necessary, facilities for large scale experiments are provided by the manufacturers. The details of the scheme are set forth in the following typical agreement, taken from a paper on "Progress in Industrial Fellowships" by Prof. Kennedy Duncan.

Agreement for Industrial Fellowships.

For the purpose of promoting the increase of useful knowledge, the University of Kansas accepts from the foundation of an industrial fellowship to be known as Fellowship.

It is mutually understood and agreed that the conditions governing this Fellowship shall be as follows:—

The exclusive purpose of this Fellowship is for the furtherance of which the holder thereof shall give his whole time and attention, with the exception of three hours a week, which he shall give to instructional work in the University.

The Fellow shall be appointed by the Chancellor of the University and the Director of Industrial Research; he shall be provided with a separate laboratory and with all supplies, reagents, &c., which could be reasonably expected to be in possession of a large University, for the cost and payment of which his lectures shall be taken in lieu. The donor, on his part, undertakes to co-operate with the University in this research in providing the Fellow with his sympathy and, on prior consideration, with his factory facilities for large scale experimentation. The Fellow shall work under the advice and direction of the Director of Industrial Research, and he shall forward, periodically, through the Director, reports of the progress of his work to the donor.

For the support of the Fellowship, which shall extend through a period of ... years, agrees to pay per year, payable annually in advance to the University of Kansas, which sum shall be paid by the University in monthly instalments to the holder of the Fellowship.

Any and all discoveries made by the Fellow during the tenure of his Fellowship shall become the property of subject, however, to the payment by him to the Fellow of an additional consideration. This additional consideration to the Fellow shall depend upon the value of the services rendered, and shall not exceed The character of this additional consideration (whether royalties, stock, or what not), its amount, the time or times of payment shall be determined by the Board of Arbitration provided for herein. At any time during the tenure of this Fellowship the holder may, at the option of the donor, take out patents at the expense of the donor, on condition that at the time of making application therefor he assigns all his rights to the donor under the conditions of this Agreement.

At or before the expiration of the Fellowship the business services of the Fellow may be secured by the donor, for a period of three years, on condition that the terms of such service are satisfactory to the parties at interest.

In the event of any disagreement between the donor and the holder of this Fellowship it is understood and agreed that such disagreement shall be settled, in so far as the dispute relates to matters of fact, by a Board of Arbitration, consisting of a representative of the University, a representative of the donor, and a third person whom these two shall select, that the decisions of this Board shall be binding upon the parties at issue, and that they shall obtain such decision before having recourse to the Courts.

It is also understood and agreed that during the tenure of this Fellowship the holder may publish such results of his investigations as do not in the opinion of the donor injure his interests, and that, on the expiration of the

Fellowship, the holder thereof shall have completed a comprehensive monograph on the subject of his research, containing what both he and others have been able to discover. A copy of this monograph shall be forwarded to the donor of the Fellowship, and a copy shall be signed and placed in the archives of the University until the expiration of three years from that date, when the University shall be at liberty to publish it for the use and benefit of the public. In the event that, in the opinion of the donor, publication three years after the termination of the Fellowship would unduly injure his interests, the donor is at liberty to appeal for an extension of time to the Board of Arbitration provided for herein, which, after consideration of this appeal, is at liberty to extend the time of publication to a period which, in its belief, conserves the interests of all concerned.

In a report on the progress of this scheme after it had been in operation for four years Prof. Kennedy Duncan states that eighteen Fellowships had been established in the University of Kansas and twenty were about to be instituted in the University of Pittsburgh, and that the results obtained by each of the Fellows whose term had expired were entirely satisfactory to the donors. In some cases the Fellowship had been extended for a further period, and in addition there had been developed a system of multiple Fellowships requiring for some one problem the intensive work of several men. The amount of the yearly stipend and the amount of the maximum bonus to be stated in the agreement were both left wholly to the discretion of the donor, with the understanding that the stipend together with the possible additional consideration determine the quality of the man that can be obtained for the work. Reviewing the results of the scheme as a whole, Prof. Duncan expresses the opinion that "from the standpoint of the industrialist this arrangement is an immense privilege, for the facilities and powers which arise from it give him results which it is safe to say could not otherwise be obtained, whilst to the young men who hold the Fellowships the arrangement gives the double opportunity both of service and of reward." A system of industrial fellowships such as that outlined above, with modifications to suit the circumstances of each case, could be instituted without difficulty in connection with the chemical schools of this country, and there can be no doubt that it would be of benefit to our chemical industries, both directly, by the investigation of questions of technical importance, and indirectly, by bringing industrial and professorial chemists into closer contact than formerly. I earnestly commend the suggestion to the consideration of all interested in chemical industry.

I feel myself precluded from dealing at any length with a subject upon which I may claim to speak with some authority, namely, the education of technical chemists, because that subject has already been discussed in an exhaustive manner by several of my predecessors, and particularly by Professor Meldola, in their Presidential Addresses. There is, however, one point to which I desire to advert very briefly. The opinions of teachers with regard to the training of chemists for technical posts are by no means unanimous, but may be grouped into three categories. Some teachers appear unwilling to admit the possibility of the existence of the chemical engineer, and maintain that the chemical student requires nothing more than a sound scientific training to fit him for an industrial career, and that, if only he is a good chemist, he will be able after he enters a chemical factory to grapple with and overcome the special problems involved in the design and construction of apparatus and plant for chemical operations on any scale. Others, again, hold that *in addition to* a thorough scientific training the student should receive such a course of instruction in chemical engineering as can be given in any teaching institution properly staffed and equipped for that purpose. Lastly, a few teachers apparently incline to the opinion that the student, after acquiring a comparatively elementary knowledge of general chemistry, should pro-

ceed at once to specialise in some branch of chemical technology. This last view I dismiss at once, because I consider it wrong in principle and futile as regards results; any specialisation in technology should be post-graduate work. The other rival methods of training stand upon a different footing, and each can be defended by cogent arguments, but my own experience leads me to advocate the second course. Probably it is true that only a small proportion of our students possess qualities of mind which enable them to become at once skilled chemists and capable engineers, but, on the other hand, it seems to me equally true that if a student has sufficient intelligence and application to become a good chemist there is no reason why he should not be able to acquire at least such a knowledge of chemical engineering as will make his path smoother when he comes to undertake manufacturing operations. The training of the technologist in pure chemistry, and to a lesser degree in physics and in mathematics, cannot be too high or too thorough—this is universally admitted—but it need not be limited to these subjects. Even at the risk of appearing to secure a gratuitous advertisement, I can best explain my own idea of a suitable course for a student who intends to devote himself to industrial chemistry by outlining the curriculum for the Associateship of the College with which I have the honour to be associated. In addition to full courses of instruction in chemistry, physics, and mathematics, this curriculum includes classes in constructional engineering, in engineering drawing, and in technical chemistry (chemical engineering). The classes in engineering and in drawing are specially arranged for students of chemistry, with the object of preparing them to enter the class in technical chemistry, which includes both lectures and laboratory work. The lectures deal with (1) the materials of construction of chemical plant, particularly with respect to their power of resisting the action of acids, alkalis, and salts under various conditions, (2) fuels, solid, liquid, and gaseous—their production, analysis, and applications, and (3) the various operations of manufacturing chemistry and the forms of plant in general use. In the laboratories, which are equipped with experimental plant and supplied with electric power, steam, and compressed air, the student receives instruction in the methods of conducting large-scale experiments, which he is required to carry out with sufficiently large quantities of material to give him an insight into industrial methods and to supply information regarding the costs and conditions of economical working on a manufacturing scale. The course also includes gas and fuel analysis, determination of the calorific value of fuels, measurements of high temperatures by means of the various types of pyrometers, experiments in gas production, and the estimation of heat losses in combustion. The full curriculum, outlined above, extends over a period of four years, during each of which the greater part of the time is occupied with work in the chemical laboratories, and on its completion the student is still required to carry out some research work in pure or applied chemistry before admission to the Associateship. Importance is attached to the last condition, because it is considered that the academic part of the training of the chemist is not complete until he has gone a step beyond routine work and has gained some experience in the methods of research. Experience has led me to the conviction that, other things being equal, a young chemist who has added chemical engineering to the other indispensable subjects of his course is a more useful man in a chemical factory than one who has to acquire all his knowledge of the subject after leaving College, and I hope that in future the opportunities afforded for the study of chemical engineering will be greater than they are at present.

Before bringing this rather discursive Address to a close I must express to the members my deep appreciation of the signal honour which they conferred in electing me President of this great Society. My year of office will not, I trust, be written down as a barren one by the future historian of the Society, but whether that be the verdict or no, I shall

always look back to it with pride and with pleasure. To the officers of the Society—the General Secretary and the Editors, past and present—I am greatly indebted for constant help in circumstances which made their work much heavier than usual, and I tender them my warmest thanks. I am also most grateful to my colleagues on the Council for the kindness and consideration which I have received at their hands. Finally, I desire to heartily congratulate the members of the Society on their choice of a new President. Dr. Carpenter's reputation as scientific man and as man of affairs stands so high as to be above commendation from me, but I lay stress on the fact that he is keenly interested in the welfare of the Society and in close touch with the important matters which have been engaging the attention of the Council. I confidently predict that his period of office will be one of distinction and of enduring benefit to the Society.

NOTICES OF BOOKS.

Petroleum Technologist's Pocket-book. By Sir BOVERTON REDWOOD, Bart., and ARTHUR W. EASTLAKE. London: Charles Griffin and Co., Ltd. 1915.

THIS pocket-book contains a great deal of useful information for prospectors, geologists, engineers, and chemists, and it is very well arranged and indexed. The requirements of the prospector are specially considered, and outlines are given of the laws governing the acquisition of oil-lands in various countries. Geological terms are defined and explained, and the mathematical tables necessary for determining depths, thicknesses of strata, &c., are provided. Tables of physical and chemical constants and analyses are given in great abundance, and in the section on methods of producing outlined descriptions are given of standard types of engines, boilers, &c. This section, and that on refining, transport, storage, &c., are both thoroughly practical. Methods of testing are described rather scantily, and fuller details might have been given with advantage. The handbook is provided with a small atlas showing the petroleum producing districts of the world, and statistics are included of the output of various countries up to the end of 1911, and in some instances for 1912 also.

Les Explosifs. ("Explosives"). By H. LE CHATELIER. Paris: H. Dunod and E. Pinat. 1915

THIS lecture, which was delivered at the Sorbonne in February of this year, gives a clear exposition of some important points connected with the modern science of explosives. The lecturer alluded to the golden dreams of the French concerning the discovery of a new explosive ten times as powerful as melinite, and emphasised the fact that no new explosives have been discovered for fifty years, but, on the other hand, the science of explosives and our knowledge of the most effectual way to use them have made enormous strides in that period. He explained methods of measuring the force of explosives, the bases of systems of classification, and the chief properties of those most commonly used. Incidentally he laid stress upon the necessity for putting all industries upon a sound scientific basis in preparation for the time when the devastations of war have to be made good, if the Allies hope to meet Germany upon anything like equal terms.

H. K. Lewis and Co., Ltd.—The business founded in 1844 by Mr. Henry King Lewis has been converted into a Private Limited Company bearing the above name. The object of the conversion is to secure the many advantages incident to incorporation, and more especially to avoid the dislocations and inconveniences which the death or retirement of any partner might cause. The conversion will not affect the general conduct of the business, which will be carried on as heretofore.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clx. No. 22, May 31, 1915.

Velocity of Reduction of Potassium Permanganate by Oxalic Acid.—A. BOUTARIC.—When a solution of oxalic acid containing sulphuric acid is added to a solution of potassium permanganate the red colour disappears rapidly but not instantaneously. Harcourt and Esson have studied the rate of the reaction, using a long and tedious chemical method, while the author has used a spectrophotometric process for the same purpose; his results, obtained with mixtures of 100 cc. of potassium permanganate solution 0.1 grm. per litre, 50 cc. of oxalic acid (50 grms. per litre), and 50 cc. of sulphuric acid (made by diluting 5 cc. to 1000 cc.), showed that in most cases the velocity of the reaction is not proportional to the quantity of permanganate in the solution, but starts at zero, increases up to a maximum, and then decreases to zero. Thus the reaction does not obey the logarithmic law. The author will publish full details of his method and results elsewhere.

No. 23, June 7, 1915.

Influence of Acetic Acid on the Synthesising and Hydrolysing Properties of α -Glucosidase.—Em. BOURQUELOT and A. AUBRY.—The influence of mineral and organic acids upon the activity of hydrolysing enzymes has been the subject of many researches. It has now been proved that some enzymes can effect two opposite reactions—that α -glucosidase, for example, can hydrolyse α -methylglucoside or determine its synthesis. The authors have carried out a series of experiments to study the influence of increasing quantities of acetic acid upon the synthesising and hydrolysing powers of this enzyme. They prepared the following mixtures:—

Aqueous solution of glucose (10 grms. in 100 cc.)	10 cc.
Distilled water	50 cc.
Methyl alcohol	15 grms.
Titrated solution of acetic acid	0.001 grm.
Aqueous maceration of yeast dried in air (10 grms. in 100 cc.)	10 cc.
Distilled water up to	100 cc.

Nine of these mixtures were prepared, the amounts of acetic acid used being 0 grm., 0.001 grm., 0.005 grm., 0.010 grm., 0.020 grm., 0.040 grm., 0.060 grm., 0.080 grm., 0.100 grm. They were allowed to stand at the temperature of the laboratory (16–20°) until the synthesis stopped. This occurred in the case of the first four mixtures, in 20 to 25 days, the amount of glucose combined being about 0.50 grm. which corresponds to the normal equilibrium. This the synthesising action is not appreciably affected if the quantity of acetic acid added does not exceed 0.01 grm. per 100 cc. In the fifth mixture only 0.317 grm. of glucose was combined, in the sixth traces only, and there was no reaction in the seventh, eighth, and ninth. To study the hydrolysis of α -methyl-d-glucoside the following mixtures were prepared:—

α -Methyl-d-glucoside	1.0777 grm.
Distilled water	60 cc.
Methyl alcohol	15 grms.
Titrated solution of acetic acid	0.0060 grm.
Aqueous maceration of yeast dried in air (10 per cent)	10 cc.
Distilled water up to	100 cc.

Six mixtures were prepared, the amounts of acetic acid used being 0 grm., 0.001 grm., 0.010 grm., 0.020 grm., 0.040 grm., 0.060 grm., and they were left in the laboratory as before. The results obtained were identical with those of the preceding set of experiments, the reaction being altogether stopped by 0.060 grm. of acid. If the acid is neutralised in the mixtures in which the reaction has stopped before equilibrium was attained, no further reaction occurs, which proves the ferment has been destroyed.

THE CHEMICAL NEWS.

VOL. CXII., No. 2905.

THE CHEMICAL ACTION OF LIGHT.

By G. CIAMICIAN and P. SILBER.

PROF. PATERNÒ has recently brought together in an article his publications on some chemical actions of light, which appeared in the *Gazzetta Chimica* in the years 1909-14, and he has added Note IX. (*Gazzetta Chimica*, vol. xlv. [ii.], p. 463), of general considerations addressed specially to us. We might refrain from making a reply because our work is sufficiently well known and does not need further comment; however, having regard to some of his observations, we think it worth while to point out that they are scarcely justified.

In 1900, resuming some old experiments (compare *Rendiconti*, 1886, January 3 and November 14), we undertook a series of systematic researches on the chemical actions of light (which had not been attempted in this way by us before), to see what were the reactions which light determines or favours in the different fields of organic chemistry. We began our studies naturally by taking as starting-point our first observations on quinine and nitrobenzene. Wishing to organise a similar large-scale research, we did not think it either useful or necessary to go over every single case, retaining a certain number of them so that we could return to those when we had the opportunity. Thus it happened that several of our subjects have often been taken up again while others have remained apparently abandoned.

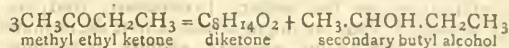
In 1909 Prof. Paternò entered this field of research. He believed that the cases examined by him were essentially different from ours, trying to show that while we have dealt entirely with phenomena of oxidation and reduction, he has undertaken the investigation of the synthetic indols. With reference to this statement we might point out that we have not found it convenient to make this distinction; in the end the formation of a pinacone is a process of synthesis, and that of triphenylethylenic glycol from benzophenone and benzyl alcohol is a process of simultaneous oxidation and reduction, inasmuch as in both the reactions light causes the passage of hydrogen from the alcohol group to the oxygen of the carbonyl; thus the first is oxidised and the second reduced. The essential fact is that light specially favours such processes, and the reactions studied by Prof. Paternò can mostly be regarded as phenomena of such a nature.

We do not of course wish to raise the question of priority, which would be out of place here. We are pleased that others should co-operate with us in a region of research in which there is employment for all. We should be satisfied if he would be willing to recognise that our modest work had the merit of attracting the attention of chemists to a subject which had been somewhat neglected. And we hope therefore that Prof. Paternò will recognise that we could not have the intention of presenting his work in a false light, and if he will allow me I will now discuss in greater detail the cases reported by him.

In our first Note (*Rendiconti*, 1901, vol. x. [i.], page 98) we had already emphasised the fact that "benzophenone is a compound which is reduced by the action of light with the greatest facility, and it is not only alcohol but also many other organic substances which transform it into benzopinacone," and Prof. Paternò has been well advised to employ this compound for his researches, which will thus complete ours. He however is mistaken in thinking that it was to the reaction with cymene and benzophenone that our observation referred, viz., that "it

does not seem to us to be justifiable to make the assumption which appears more or less clearly in Prof. Paternò's publication that the reactions described by him are essentially different from ours." No; in this case it was not a question of an experiment essentially different from ours, but of an experiment which Prof. Paternò had repeated without obtaining anything more than we had observed. In fact in our fifth Note we said that "to discover what alteration the cymene has undergone it is necessary to repeat the experiment on a much larger scale." Prof. Paternò has repeated it, but, like us, with 3 grms. of benzophenone and 10 grms. of cymene, and has not been able to recognise the second product which is formed besides benzopinacone. Taking up the study again with 50 grms. of each of the two compounds, we found (Note XVII., these *Rendiconti*, vol. xix. [i.], page 645) that this product is a diacymenyl. It is true that we published these results fifteen and a half months after Prof. Paternò's work appeared. By his work he called our attention to our old experiments, and we tried to complete them in details in which he had not done so. Thus from benzophenone and toluene we obtained dibenzyl, which had escaped him.

Regarding the formation of the diketone $C_8H_{14}O_2$ from methylethyl ketone, we said that "this is an unexpected and really noteworthy result," because methyl ethyl ketone, unlike acetone, reacts with itself according to the equation—

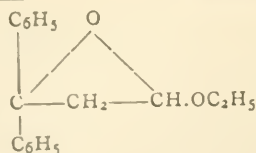


being reduced to secondary butyl alcohol and oxidised to diketone, the latter being an interesting compound owing to its relation to tetramethylpyrrol. Willstätter (*Ber.*, 1914, xlvii., p. 293) is of the same opinion.

The observation of Prof. Paternò relative to the fundamental reaction which takes place with benzophenone and benzyl alcohol in the formation of triphenyl ethylene glycol is very strange. He says: "They (we) add, as a proof that they have no clear insight into the reaction, that the formula of triphenyl glycol itself needed further experimental proof before being accepted." Now this reservation of ours was caused by a bibliographic mistake, for it escaped us that triphenyl glycol was already known; in fact, in our detailed memoir, published in the *Gazzetta Chimica* (1904, vol. xxxiv. [ii.], page 133), we said:—"This substance is very probably identical with that obtained and described by A. Gardeur, to which this author ascribes the melting-point 164°. (We found 168°). Both his and our experiments show clearly that it has the constitution of triphenyl-glycol, the formation of which by light by the condensation of benzophenone with benzyl alcohol is an interesting fact, although capable of being foretold from our work."

Prof. Paternò ought not to be astonished if after the publication of many other cases of the same type on his part we have again taken up our studies on aldol and enol condensation, as he calls it. We were quite within our rights, and it is for that reason that we wrote (as is stated above) that the photochemical reactions described by him were not essentially different from ours; it appears that we may have been rather modest.

With regard to the reaction with benzophenone and ether we have refrained from recording the experiments of Prof. Paternò on the subject for various reasons—first of all because he has not mentioned ours performed in 1901 (see our Memoirs in the *Atti della R. Accademia delle Scienze di Bologna*, 1901, and in the *Gazzetta Chimica*, xxxii. [i.], p. 1557), in which we had shown that benzophenone is transformed into pinacone and a resinous substance, of which we said that we could not obtain it in a state of sufficient purity, but into the composition of which ether entered. Prof. Paternò, repeating after nine years the same experiment, did not obtain anything different, for his resin, to which he attributed with reservation the formula—



which gives 12.3 per cent of oxyethyl, while the formula requires 17.7 per cent. Its molecular weight would be 254, while the value found was 310. He said therefore that these results "prove that the substance was not by any means pure, and that it still contained benzopinacolone."

We on repeating our original experiment (*Rendiconti*, xx., [i.], 723; *Ber.*, xlv., 1557) found, besides benzopinacolone and the resin, a crystalline product which melts at 51°; to this we ascribe the formula $\text{C}_{17}\text{H}_{20}\text{O}_2$ —i.e., that of an addition product. With regard to the resin, we confine ourselves to saying that its formation must be connected with that of benzopinacolone without proposing a formula, although we have determined the molecular weight (363 to 372) and the percentage of oxyethyl (14.80).

Having less confidence about the resin, the formula proposed by Prof. Paternò seems to us premature, and it was for the sake of not making these observations that we refrained from referring to his work.

The resins present well known difficulties—as is shown by our repeated experiments on the polymerisation of benzoic aldehyde, but we may mention that in our first publication on the subject (*Rendiconti*, 1901, i., p. 99) we said, "Thus we might attribute to it the formula $4(\text{C}_{14}\text{H}_{14}\text{O}_4)$. We do not, however, venture to do this, and we are aware of the fact that the agreement of the numbers may be fortuitous." The later research (*Ibid.*, 1903, i., p. 236, and 1909, i., p. 216) constitutes a regular resumption of a study for which nobody can blame us. Prof. Paternò may believe that the reason we find ourselves in conflict with him is because his researches are being made in a field of study which is sometimes too near our own.

Finally, we wish to complete an observation made in our last Note (*Ibid.*, 1914, i., p. 864). It deals with the action of light on mixtures of ethyl alcohol and acetic aldehyde, from which, as we had foreseen in an earlier paper (*Ibid.*, 1911, i., p. 715) dimethylethylenic glycol ought to be formed. Prof. Paternò and G. Peret (*Gazzetta Chimica*, 1914, xlv., [i.], p. 152) have performed the experiment without arriving at a definite conclusion.

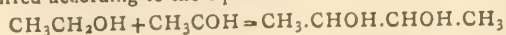
We exposed in tubes mixtures of the two substances, consisting of 345 cc. of alcohol and 55 cc. of acetic aldehyde, from March to September, 1914. The product was first distilled on the water-bath and then with aqueous vapour. On salting out with potassium carbonate, from the yellow residue of the distillation (24 grms.) an oily liquid (13 grms.) of the same colour is separated; at 26 mm. it passes over between 100 and 110°. The first portions contain small quantities of diacetyl, which can be recognised by its dioxime of melting-point 240°.

The principal portion, which at ordinary pressure is obtained from 178–185°, boiling chiefly at 182°, consists of dimethylethylenic glycol, the boiling-point of which is given as 183–184° ("Beilstein," 3rd edition, vol. i., p. 262).

Analysis.	Found.	Calculated for $\text{C}_4\text{H}_{10}\text{O}_2$.
C	53.67	53.33
H	10.81	11.11

To prove the identity we oxidised with bromine water in the light and obtained diacetyl, which was recognised by means of its dioxime of melting-point 240°, which gives the characteristic salt of nickel (see Tshugaeff, *Ber.*, xxxviii., p. 2520).

Thus—as we had foreseen and as Prof. Paternò had afterwards shown was probable—the reaction really occurred according to the equation—



and thus the series of reactions which occur with ethyl alcohol and acetone in light is completed (*Rendiconti*, 1911, xx., [i.], p. 720).—*Rendiconti della R. Accademia dei Lincei*, 1915, xxiv., [i.].

THE FUNDAMENTAL PRINCIPLES UNDERLYING THE CHOICE OF STANDARD WEIGHTS FOR THE ELEMENTS.

By JOHN WADDELL, B.Sc. (London), D.Sc. (Edinburgh).

STUDENTS of chemistry, even after having worked at the subject for two or three years, often show the crudest and most vague ideas regarding the principles upon which rest the standard numbers for the different elements—the so-called atomic weights. Probably nine out of ten of them, if given the percentage composition of several compounds of two elements and asked to show that these compounds conform to the law of multiple proportion, will make use of the ordinary atomic weights in the proof. If the names of the elements are not given, the data are considered insufficient and the problem is unsolved. It is not realised that the law is a *statement of a fact of nature*, that the fact existed long before its discovery, and that the proof of the fact cannot depend upon any *arbitrary* value that we assign to the elements. Indeed, it is vaguely, if at all, realised that the numbers are arbitrary. Many students think that $\text{Cl} = 35.5$ or $\text{Na} = 23$ is as much a property of the substance, as that the former is a yellowish green gas of very irritating action on the mucous membranes, or the latter is a brilliant white metal lighter than water. It is with a view of helping students, and possibly teachers also, that this article is written.

The student learns that there are so-called chemical laws, the law of constant proportions, of multiple proportions, and of reciprocal proportions; but he learns them as isolated statements, and has no conception of their bearing upon the science of chemistry and of chemical theory.

It should be noted in the first place, that if the law of constant proportions did not hold, no calculation of chemical quantities would be possible. If one specimen of common salt contained one-third its weight of chlorine, another one half, another one-fifth, or any haphazard amount, it is evident that the manufacturer would not know how much salt he would need in order to make a ton of chlorine. It is also evident that if a definite quantity of sodium, such as a grm. or an ounce, were taken as a standard and represented by a symbol which might be a square, or a cube, or a sphere, or a letter, it would be impossible to represent a standard quantity of chlorine, since there is *no* standard quantity, the quantity of chlorine combining with the standard quantity of sodium varying in a fortuitous manner.

So, also, if water contained at one time eight, at another nine, at another ten times as much oxygen as hydrogen, it would be impossible to fix on *standard* quantities for *both* oxygen and hydrogen. If, then, the law of constant proportion did not hold, it would be impossible for us to have a set of standard quantities for the different elements.

But if the law of reciprocal proportions (sometimes called the law of combining weights) did not hold it would be equally impossible to compile a set of standard weights for the elements. Suppose, for instance, that one part by weight of hydrogen unites with seven parts by weight of oxygen and with thirty parts by weight of chlorine, but that thirty parts of chlorine unite not with *seven* but with *nine* parts of oxygen; it is evident that though the standards for hydrogen and chlorine may be taken as unity and thirty there is no standard possible for oxygen. Seven and nine would have equal claims, and the more numerous the compounds of oxygen examined the greater might be the confusion.

If the law did not hold it would not be possible, by

knowing how one element united with each of two others, to predict how these two elements would themselves unite. An illustration is afforded by the case of alcohol, water, and ether. Alcohol mixes in all proportions with water, and in all proportions with ether, but ether and water are far from mixing in all proportions. Water will dissolve a little ether and ether will dissolve a little water, the quantity dissolved by an equal amount of solvent being different in each case. A universe is conceivable where there would be no law of constant or of reciprocal proportions, and if such a universe were made up of different elements it would be impossible to have symbols as we now do for the elements.

It is because these laws are found to hold that the atomic theory is possible. Indeed, if there are two atoms in the usually accepted sense the laws must hold. The converse is not necessary. It does not follow that because the laws are a correct statement of fact atoms must necessarily exist, any more than it would follow that because two solutions look alike and can neutralise an acid they necessarily contain the same substance in solution.

But now, assuming the laws, how do we arrive at standard numbers for the elements?

The law of constant proportions refers to weight; *four grms.* of sulphur unite with *seven grms.* of iron. Shall we make the standard weight of sulphur 4 grms. and the standard weight of iron 7 grms.? Or shall we make the standard quantity of sulphur unity and the standard quantity of iron 1.75? It would be possible to make either choice, and since sulphur and oxygen unite in equal quantities the standard quantity of oxygen would be four, or unity, according to the choice that we make.

On the other hand, the quantity of iron might be called unity, in which case the standard number for sulphur and for oxygen would be 4/7. So we see the standard numbers will depend upon the element we choose as the primary standard and the value we assign to the standard quantity of it.

But now we are confronted with the question whether either sulphur or iron is the best element to choose as the primary standard. If we consider first what elements are obviously unsuitable, it may be more easy to decide what are suitable. Obviously the very rare elements, such as radium, scandium, or praseodymium, are unsuitable because of their rarity and cost, if for no other reason. Obviously, also, any member of the argon group of elements is unsuitable, if for no other reason, because they do not form compounds with other elements. It is plain, then, that the element chosen as original standard must be plentiful and must form compounds with a number of other elements. It should also be possible to obtain it practically pure. The elements that form water have these characteristics, and these elements hydrogen and oxygen have both been chosen as the standard. Hydrogen has the advantage that it enters into combination in the smallest quantity of any of the elements, and so if the standard quantity of it is taken as unity the standard quantities of all the other elements will be greater than unity. Oxygen has the advantage that it combines with more elements than does hydrogen, forming compounds with nearly all the elements. Dalton chose to make hydrogen the standard. Berzelius made oxygen the standard. The value given to hydrogen was naturally unity, Berzelius chose to call the standard quantity of oxygen 100. Since the quantity of oxygen in water is approximately eight times the quantity of hydrogen, if oxygen is taken as 100, hydrogen is approximately 12.5, and the number in the list of standard quantities for the different elements according to Berzelius's plan of making the standard quantity of oxygen 100, would be 12.5 times as great as those determined upon Dalton's basis. The standard of hydrogen equal to unity was considered most convenient and was generally adopted.

Now, if hydrogen were taken as unity, and if hydrogen formed one compound and only one with every element, it

would, theoretically at least, be very easy to determine numbers for the standard quantities of each of the other elements, it being understood that the law of reciprocal proportions holds good. But the fact is that hydrogen does not form compounds with all the other elements, and with many elements it forms more than one compound. The first difficulty can be got over. The standard quantity of calcium, for instance, could be arrived at if the quantity of oxygen which unites with unit quantity of hydrogen is known and the quantity of calcium with which this quantity of oxygen will unite. Suppose eight parts of oxygen unite with one part of hydrogen, and eight parts of oxygen unite with twenty parts of calcium, the standard quantity of calcium is evidently 20.

A still greater difficulty is caused by the fact that elements frequently combine in more than one ratio forming more than one compound. Hydrogen, for example, unites with sixteen times its weight of oxygen as well as with eight times its weight. Should the standard quantity of oxygen be 8 or 16? This question caused difficulty for a long time, and so long as *weights only* were considered the problem was unsolvable.

Solids and liquids have no definite and general relationship between their weight and volume, but gases have, and so our formulæ for gases can be made to represent volumes as well as weights, and if our standard numbers for weight can be suitably fitted to volumes a decided advance may be made, assuming that 1 gm. of hydrogen has been taken as standard weight, and is represented by some symbol such as H, a very natural volume to choose as the fundamental standard would be the volume of 1 gm. of hydrogen which at the normal temperature and pressure is approximately 11.2 litres. Now, if H is the standard quantity, the standard quantities of all gases containing hydrogen must have a certain number of these standard quantities of hydrogen, one or two, or three or four, &c., H. If 11.2 litres is to be the standard volume, 11.2 litres of all gaseous compounds of hydrogen should contain 1, 2, 3, or 4, &c., grms. of hydrogen. This turns out to be true for many compounds of hydrogen, such as sulphuretted hydrogen, marsh gas, and ethylene, but not for phosphoretted hydrogen, ammonia, and hydrobromic acid, and a number of others. If, however, 22.4 litres be taken as the standard volume the difficulty disappears. 22.4 litres of ammonia and of phosphoretted hydrogen have in their composition 3 grms. of hydrogen, and 22.4 litres of hydrobromic acid contains 1 gm. of hydrogen, and there is no gaseous compound of hydrogen known which has not in that volume some integral number of grms. of hydrogen; that is, the standard *volume* of the gas contains some integral multiple of the standard *weight* of hydrogen. Now, if this same volume, 22.4 litres, be chosen for the gaseous compounds of oxygen, it will be found that the oxygen contained is always some multiple of 16. In the same way 22.4 litres of gaseous nitrogen compounds contain some integral multiple of 14 grms. of nitrogen.

Now, the point to be decided regarding the standard of oxygen was whether it should be 8 or 16, because these are the ratios in which it combines with the unit weight of hydrogen. In the same way the question regarding nitrogen was whether it should be 14 or some multiple or submultiple of 14. It will be seen that the experiments with gases give the preference to 16 and 14 as the standard quantities of oxygen and nitrogen. The same reasoning applies to all those elements that give gaseous compounds easily worked with, and so their most satisfactory standard numbers are deduced.

If 100 grms. of oxygen had been taken as the standard weight of that element, the volume would have been different, namely, 6.25 times as great, but the reasoning would be exactly the same.

It has been assumed up to now that the weight of oxygen in water is exactly eight times that of the hydrogen. This is not exactly the case, but more nearly 7.94 times as much, and if the standard weight of hydrogen is taken as

unity the standard weight of oxygen would be not 16 but 15.88 nearly. Now, many more elements combine with oxygen than with hydrogen, and the ratio of the element to oxygen is more often determined than the ratio to hydrogen, and if the number assigned to the element is to be compared with hydrogen as unity it is evident that the ratio to oxygen must be multiplied by 15.88. If there is any error in the ratio of oxygen to hydrogen this error would appear in the other elements being greater as the standard number is greater, so that in the case of uranium the oxygen error would be multiplied by 15. Hence it is now usual to make oxygen the standard, but instead of 100, as selected by Berzelius, the standard quantity is taken as 16. This gives the standard quantity of hydrogen as 1.0075 instead of unity. This small difference does not usually need to be considered. One advantage of taking the standard quantity of oxygen as 16 is that the standard quantities of most of the other elements are sufficiently near whole numbers that these whole numbers may for most purposes be taken as exact. It is to be clearly understood that making the standard quantity of oxygen 16 arose from making the standard quantity of hydrogen unity. No one would naturally have chosen 16 as the standard quantity of oxygen in the first instance.

It may be asked whether the law of Dulong and Petit does not give our present atomic weights—does not decide, for instance, whether the standard quantity for iron shall not be 56 instead of 28 or 7, as was suggested early in this article. Would not Dulong and Petit's law preclude oxygen being taken as 100 and the standard of iron 350? The reply is, not at all! Dulong and Petit's law is often given in the form that the product of the atomic weight multiplied by the specific heat of an element is approximately 6.4. This, however, is not really the law. With the set of standard weights that we have adopted for the different elements the product of these standard weights and the specific heats is approximately 6.4, and if any new element were discovered and its specific heat determined the number which would be chosen for the standard weight would be that which multiplied by the specific heat would most nearly approach 6.4. But this is because we have already fixed upon the standard weights for the other elements. If all the other standard weights were half their present value the product would be 3.2; if they were double, the product would be 12.8. All that Dulong and Petit's law asserts is, that the standard weights of all the elements shall be so chosen that the product of the standard weight into the specific heat will be approximately constant. All the standard weights must conform; the product in all cases may (so far as this law is concerned) be 3.2 or 6.4, or 17 or 100, or any other number, but it is not allowable for the product to be in one case 3.2, in another 6.4, in another 17 or 19, or 100.

The Periodic Law would also be unaffected if the value assigned to the primary standard, provided the ratio between the standard weights is kept the same as now. The Periodic Law would be interfered with if calcium were given a value 20 while potassium was kept at 39, but if the value of potassium were halved or doubled the Periodic Law would be undisturbed, provided the present numbers for all the other elements were correspondingly halved or doubled.

The line of argument presented above is not difficult to follow if the student's mind is not prejudiced by wrong impressions already received or misconceptions already formed. This treatment of the subject should be introduced before the atomic theory, but not till some familiarity is obtained with simple experimental phenomena. Water, hydrogen, oxygen, hydrogen peroxide, ozone, air, nitrogen, ammonia, nitrous oxide, nitric oxide, carbon dioxide, and carbon monoxide may well be experimented with and their properties discussed as a beginning in the study of chemistry. Incidentally, the difference between a mixture and a compound will be noticed, and facts may be learned which may be used to lead up to the laws of

chemical combination and hence to formulæ. In order to change the symbol weight of an element to atomic it is only necessary to introduce the atomic theory, and Avogadro's law will allow the standard formulæ for gases to be translated into molecular formulæ. The student should be made to thoroughly realise that Avogadro's law is not a law in the same sense as the laws of constant, multiple, and reciprocal proportions, but that they are statements of fact, while it is merely the statement of a theory; a theory, indeed, in accordance with all the facts so far known, but nevertheless a theory.

School of Mining, Kingston, Canada.

ON THE PHYSIOLOGICAL ACTIVITY OF COMBINED HYDROCHLORIC ACID.*

By J. H. LONG.

THE question of the efficiency of hydrochloric acid, when combined with different compounds in the digestion of proteins by pepsin, has received much attention in earlier years, but has been settled only in a very general way. The acid combined with inorganic bases is of course inactive in this direction, but as to the behaviour of proteins or protein derivatives in combination there was and there is yet some dispute.

The early discussions of the question we find between 1880 and 1890, when by the introduction of new indicators the conception of acid held by protein could be more easily followed. Slightly earlier than this Hoppe-Seyler had made the observation that hydrochloric acid gradually combines with the products of peptic digestion, and that the rapidity of digestion diminishes because of this combination ("Physiologische Chemie," 231). Danilewski in 1880 (*Maly's Jahresber.*, 1880, x., 5; *Liebig and Kopp's Jahresber.*, 1880, 1033) discusses the nature of this acid combination, and refers the property to the gradual formation or liberation of bodies of amine character. With the progress of digestion the amounts of these would increase. To follow the changes in the amount of free acid or free alkali after treatment of protein with an excess of either he recommends the use of tropæolin oo and boo. His observations were somewhat inexact, however.

The use of phloroglucin and vanillin mixture as an indicator for "free" acid was introduced by Guenzburg in 1887 (*Centralbl. klin. Med.*, 1887, ix., 185) and the sugar and resorcinol mixture by Boas a little later (*Ibid.*, 1887, ix., 817). Congo-red seems to have been recommended for physiological investigations somewhat earlier. Through the aid of these indicators it became possible to study much more conveniently the behaviour of hydrochloric acid in artificial digestion processes as well as in the stomach. The distinction between the behaviour of phenolphthalein and methyl orange in the titration of digestion mixtures was gradually cleared up.

It was shown by Von Pfungen (*Maly's Jahresber.*, 1889, xix., 240) and others that the hydrochloric acid which combines with protein is so loosely held that it may be dissociated more or less readily by dilution with water although there is no separation by dialysis. For this reason the proposed method for the recognition of free hydrochloric acid by the addition of cinchonine and extraction with chloroform must be of no value in the separation of actually free hydrochloric acid in excess over the protein. However, the differences in behaviour between the more complex proteins and their derivatives or digestion products was not at this time recognised.

An important addition to the methods for the identification of actually "free" acid was made by F. A. Hoffman when he proposed to employ the speed of the inversion of

* This investigation has been made with the assistance of a grant from the Committee on Therapeutic Research, Council on Pharmacy and Chemistry, American Medical Association. From the *Journal of the American Chemical Society*, xxxvii., No. 5.

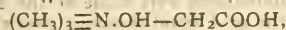
cane sugar as a measure of acidity present in such cases where protein is concerned (*Centralbl. klin. Med.*, x., 793; xi., 521; *Maly's Jahresber.*, 1889, xix., 256; 1890, xx., 234). The method had been used successfully in other mixtures. In these papers the notion of mass action in the combination of acid and protein is brought out sharply, as well as the disturbance through dissociation by water. Substances like peptone hydrochloride and betain hydrochloride dissociate in water and permit the acid to act as physiologically free, but substances like quinine hydrochloride, on the other hand, hold the acid in such combination that it is not available for peptic digestion. The distinction is brought out by E. Salkowski and M. Kumagawa, who were able to show that hydrochloric acid combined with leucine or other amino acid, so as to form a chemically neutral salt, is still physiologically active, since in aqueous solution the acid leaves the leucine and promotes peptic digestion (*Virchow's Archiv.*, 1890, cxxii., 235).

In a later publication, following criticism of this point of view by Rosenheim (*Maly's Jahresber.*, 1891, xxi., 221) and Hoffmann (*Ibid.*, 1891, xxi., 204), Salkowski (*Virchow's Archiv.*, 1892, cxxvii., 521) goes more fully into the subject, and shows the conditions under which the hydrochloric acid may become inactive. This follows when a very large amount of egg albumin or fibrin is digested with a limited amount of the leucine hydrochloride or similar substance. It might have been pointed out that digestion with ordinary free acid would be very slow or might even fail under the same conditions. This last view is a contradiction of the one advanced by Schiele (*Maly's Jahresber.*, 1895, xxv., 272), according to which the only active acid is that which is already in combination with protein. The so-called free acid would be useful only in combining with the digestion products formed beyond the albumose stage. As these products of hydrolysis are formed more and more acid will be taken up. Any excess of acid beyond this may be harmful, or at any rate unnecessary.

The rather numerous investigations which have appeared on the question of the behaviour of combined hydrochloric acid leave a number of points still undecided. The real activity of the acid in presence of an excess of protein calls for a fuller study, and especially by aid of the electrometric methods which permit a determination of true acidity without the introduction of anything to disturb existing conditions of equilibrium. In the work to be described below the digestive activity of hydrochloric acid combined with certain amino acids on the one hand and with complex proteins on the other is compared. As the experiments in this investigation are practically all comparative, digestion is measured by the simple means of filtration and Kjeldahl determinations of the soluble nitrogen. For the purpose this affords a satisfactory measure of what may be called "digestion."

I. The Behaviour of Betain Hydrochloride.

This substance was chosen to illustrate the behaviour of an amino acid-like body because of its comparatively simple structure and the ease with which it may be obtained in pure condition. It may be secured from chemical dealers, and at the present time is obtainable also in nearly pure form under the name of *acidol* from one of the large German chemical companies. The original source is the residue from beet-sugar manufacture. The free hydrate has been given the formula—



while the hydrochloride is $\text{Cl}(\text{CH}_3)_3\text{N} - \text{CH}_2\text{COOH}$. For the experiments below the commercial product was crystallised from hot alcohol. The purified salt, on titration with 0.1 N alkali and phenolphthalein, gave a sharp result for the halogen acid present. The end point in the titration with methyl orange is nearly as sharp, but the volume of alkali added is slightly less; in other words, the basic behaviour comes slightly in evidence here. The

titration with alkali and phenolphthalein is complete. What is the actual [H] ion concentration in solutions of this salt? To determine this a series of solutions were made to contain definite amounts of HCl. These solutions were used in digestion experiments to be given. The hydrochloride used as crystallised above had a purity of 98.2 per cent, shown by silver and alkali titrations.

In preliminary experiments on the rapidity of digestion by aid of pepsin I used in one instance 5 grms. of fibrin with 4.42 per cent of nitrogen, 50 mgrms. of pepsin, 500 mgrms. of the hydrochloride, and 50 cc. of water. The mixture was digested at 40°. In two hours the reaction was far advanced, with most of the fibrin in solution, but it was continued fourteen hours longer, sixteen hours in all. The mixture was boiled and filtered, the residue being well washed. In the filtrate the soluble nitrogen was found to be 231.7 mgrms. as the mean of two experiments. This is greater than the total nitrogen of the fibrin, but must be diminished by the nitrogen of the betain hydrochloride and the pepsin, 45.5 mgrms. $231.7 - 45.5 = 186.2$. As the total fibrin nitrogen was 221 mgrms. the result shows a digestion value of 84.2 per cent.

In a similar experiment with eggs I employed the coagulum from 1.2 gm. of egg albumin powder containing 70 per cent of dry protein. In the mean of two experiments the nitrogen found was 131.6 mgrms. This must be diminished by the nitrogen of a blank experiment in which killed pepsin was used. At the end of each digestion the mixtures were exactly neutralised with sodium hydroxide, boiled, and filtered. In this way the neutralisation precipitate was excluded. $131.6 - 44.1 = 87.5$ mgrms. of nitrogen from the more advanced digestion, which was practically completed in two hours, but which was continued over night as above.

These experiments indicate an advanced degree of digestion, and nearly as much as would have been obtained by the use of the equivalent amount of free hydrochloric acid.

For most of the experiments detailed below a solution was used which contained 10.69 grms. of the betain hydrochloride dissolved in water to make 500 cc. This corresponds to 2.5 grms. of actual HCl in the water volume, or 25 mgrms. HCl to 5 cc. of solution.

Experiments were now made with a constant volume of liquid, weight of pepsin, weight of egg, but variable acid product, the digestions being carried uniformly through four hours. In each test the weights were as follows:—

Coagulum from 1.5 gm. egg albumin = 1.06 gm. protein.

Pepsin 15 mgrms. in 30 cc. solution.

Liquid volume made always to 60 cc.

At the end of the digestion, conducted at 40°, the mixtures were boiled and filtered. The slight residues were well washed and the total filtrates used for nitrogen determinations. The volumes of betain hydrochloride solution taken contained the equivalents of 25, 50, 75, 100, 125, and 150 mgrms. of actual HCl, and would furnish, therefore, a considerable amount of nitrogen to the filtrate. The volume in test A was 5 cc., containing 106.9 mgrms. of the hydrochloride, and therefore 9.6 mgrms. of N. This weight is subtracted from the result of the Kjeldahl, and corresponding amounts in the other tests. The pepsin N is too small to be noted here.

The results of the Kjeldahl determinations are given below, and the values are corrected for the betain hydrochloride N. It is assumed that all the nitrogen from this source came through in the filtrate, which is probably correct for a test carried out in this manner. When neutralisation is effected before filtering, however, some of the betain may be separated and precipitated with the neutralisation product.

A parallel set of experiments was carried out, using free hydrochloric acid in place of the betain hydrochloride of Table I. The conditions of the tests were otherwise the

same. It was observed that the digestions began somewhat earlier, and for a time appeared to be more marked than with the betain salt. At the end of the period of four hours the extent of the digestion in the two cases was nearly the same, with the advantage slightly in favour of the free acid, as shown in Table II.

TABLE I.

	Cc. betain HCl sol.	Total N.	Betain N.	Net N.	Protein.
A	5	0.0157	0.0096	0.0061	0.0381
B	10	0.0806	0.0192	0.0614	0.3838
C	15	0.1530	0.0288	0.1242	0.7762
D	20	0.1874	0.0384	0.1490	0.9313
E	25	0.1961	0.0480	0.1481	0.9256
F	30	0.2079	0.0575	0.1504	0.9400

TABLE II.

	Mgms. HCl added.	Soluble N.	Protein.
A	25	small, not determined.	
B	50	0.0980	0.6125
C	75	0.1422	0.8887
D	100	0.1410	0.8812
E	125	0.1526	0.9538
F	150	0.1618	1.0112

As showing, further, the rapid digestive action of the betain hydrochloride, experiments were made with fibrin as with the egg. In each test 3.9 grms. of fibrin, equivalent to 1.06 grms. of protein, were used. The total liquid volume was 60 cc., containing varying amounts of the betain salt and 15 mgrms. of pepsin. The digestion time was three hours at 40°. At the end of the time the mixtures were boiled, diluted, and filtered for the Kjeldahl determinations. The results of the tests are given in Table III.

TABLE III.

	Cc. betain HCl sol.	Total N.	Betain N.	Net N.	Protein.
A	5	0.0462	0.0096	0.0366	0.2287
B	10	0.1496	0.0192	0.1304	0.8150
C	15	0.1824	0.0288	0.1536	0.9600
D	20	0.1869	0.0384	0.1485	0.9281
E	25	0.1995	0.0480	0.1515	0.9468
F	30	0.2160	0.0575	0.1585	0.9906

The digestions progressed very rapidly, and it is evident that the salt dissociates largely and in amount sufficient to produce a change in the protein almost comparable with that of the free acid. That some of this separated acid goes at once into combination with the protein is suggested by the following experiment:—

The coagulum from 1.5 gm. of egg powder, representing about 1 gm. of true protein, was mixed with 30 cc. of the betain HCl solution, containing 150 mgrms. of the acid. The mixture was shaken through two hours to effect complete combination. (Data, to be given in another paper, will show something about the rapidity of combination of weak acid with protein). At the end of the shaking the mixture was filtered and the solid residue washed with about 30 cc. of water. The filtrate, titrated by aid of methyl orange, required 22.6 cc. of 0.1 N NaOH, while 30 cc. of the original required 40.8 cc.; therefore $40.8 - 22.6 = 18.2$ measures the acid held, about 66.4 mgrms., for the gm. of protein. This is essentially the amount which would have been taken up from a weak solution of free hydrochloric acid.

In two similar experiments portions of coagulum from 1.5 gm. of egg were mixed with 20 cc. of the betain hydrochloride solution and 50 cc. of water and shaken through one hour, but not as actively as before. The mixtures were filtered, the residues being washed as before. In one filtrate the HCl required 19.6 cc. of 0.1 N silver nitrate, equal to 71.5 mgrms. of the acid, while in the other filtrate 19.5 cc. of 0.1 N NaOH were needed to neutralise the acid. The results agree in showing that

28.5 mgrms. of HCl had been taken by the protein in this case, where the original concentration of the acid was much stronger than in the first test.

It is desirable to know the actual concentration of the active hydrochloric acid in these solutions used for the digestion experiments—that is, the (H) concentration. Attempts were made to determine this in two ways—first, by the use of a series of indicators, as suggested by Friedenthal, Salm, and others, and perfected by Soerensen, and, second, by the measurement of the electric potential in concentration cells. This method seems to give much better results than could be secured by the indicator titrations, and was finally followed for all the tests. Cells of the Hamburger type were used for a time, but were later given up in favour of the Hasselbalch cell and the 0.1 N calomel electrode, as recommended by Soerensen (*Biochem. Zeit.*, 1909, xxi., 131; *Ergeb. der Phys.*, 1912, xii., 393). The much easier correction for the diffusion potential is a point of great practical importance here, and for this purpose observations were made with 3.5 N and 1.75 N KCl, as a connecting bridge between the concentration cell and the calomel electrode.

For the sake of comparison and to test the general accuracy of the method, I made a series of determinations of π_0 , the potential of a true normal solution, at 18°, following the Soerensen procedure. This I found to be 0.3381 at 18° and about 0.3379 at 20°, which is a trifle higher than the Soerensen value, viz., 0.3377. I kept the temperature as nearly as possible at 20° during the tests, and therefore took—

$$P_H = (\pi - 0.3379) / 0.0582$$

as the formula for reduction generally employed. For higher temperatures the denominator is a little larger, and is practically 0.0002 more for each degree. (The whole denominator is 0.000987T, where T is the absolute temperature). As the P_H is the common logarithm of the reciprocal value of the (H) concentrations of the solutions, the latter is easily calculated.

Determinations made on the solutions of the same strength as were employed in the digestion experiments gave these results. The figures given under "theory" show the (H) concentrations on the assumption that the HCl is fully separated from the salt and completely dissociated.

TABLE IV.

	Cc. betain HCl sol.	H ₂ O.	P_H .	C_H .	Theory. C_H .
A	5	55	2.067	0.0085	0.0114
B	10	50	1.868	0.0135	0.0228
C	15	45	1.753	0.0176	0.0343
D	20	40	1.656	0.0220	0.0456
E	25	35	1.592	0.0256	0.0571
F	30	30	1.534	0.0292	0.0686

The experimental results are very interesting. The weakest solution is slightly more than 0.01 N, while the strongest is less than 0.1 N. It must be remembered that the betain hydrochloride is dissolved so as to make in 5 cc. the equivalent of 25 mgrms. of HCl, and each solution was diluted to 60 cc. with pure water before each test. As the dissociation in the 0.01 N HCl is not far from 95 per cent, it will be seen that in the weakest solution the (H) of the mixture is about 85 per cent. of the theoretical. In the strongest solution the (H) concentration is about 46 per cent. of the theoretical.

Several determinations were made of the concentration of the (H) in the acid liquid standing over egg coagulum at the outset of digestion, or before pepsin is added. Two tests are sufficient to illustrate this condition. In the first, 10 cc. of the above betain hydrochloride solution (= 50 mgrms. HCl) were mixed with 50 cc. water and the coagulum from 1.5 gm. of egg. In the second case, 30 cc. of the same acid solution were mixed with 30 cc. of water and the 1.5 gm. of egg. The mixtures stood two hours with frequent shaking and were then filtered.

The potential tests were made on the filtrates, with these results:—

	Cc.	P _H .	C _H
1.	10	2.259	0.0055
2.	30	1.745	0.0179

In the first case the concentration of the acid left is about what comes from the dissociation of a protein hydrochloride in excess of water. In the second case the hydrogen ion concentration is reduced to that of an original solution of 15 cc. of the betain hydrochloride. The grm. of protein has taken up approximately 7 per cent of acid and the supernatant liquid exhibits clearly the excess.

In ordinary digestion experiments, in which a protein-like egg albumin is dissolved by pepsin and hydrochloric acid, the concentration as well as the total amount of the latter come into play. We speak of a 0.2 per cent acid as being a good concentration, and this is true provided the total amount of acid is more than enough to combine with all the protein. In the usual test to measure the activity of pepsin, as given in the U.S. Pharmacopœia, for example, we have a mixture containing about 1.25 grm. of real protein with one-tenth its weight of actual HCl in 40 cc. of liquid. The original concentration of the acid is therefore about 0.3 per cent, but approximately one-half of this is taken up by the protein, leaving a residual concentration of 0.15 per cent, which is probably more than is required for maximum activity. From the experiments above with betain hydrochloride, as well as with free HCl, it is seen that digestion is rapid in a far lower concentration.

(To be continued).

CO-PARTNERSHIP IN CHEMICAL INDUSTRIES.*

By Sir WILLIAM H. LEVER, Bart.

You have invited me to say a few words on the subject of Co-Partnership in relation to the Chemical Industry, and I have welcomed the opportunity you thus gave me of doing so, although it has not been a duty easy of fulfilment, owing to the fact that we are living in war times, and that during war a greater demand is made upon the time of each of us than when we are following the routine details of our business under the normal conditions of stable peace.

Lessons of the War.—There is an old saying—"In times of peace prepare for war." I think the opposite of this is more applicable to-day, and is no less true—"In times of war prepare for peace." The industry with which you are all connected, and of which the soap business is a branch, is known as the chemical industry; and we have become accustomed to hear it stated on public platforms and in the public Press that we British have allowed the Germans to acquire the lead in the fields of chemical industry. When we examine into these claims we find that it is not because the Germans have originated more inventions, or made more important discoveries, than either we British or our Allies—the French. On the contrary, we find that the initial genius of inspiration has not been of German origin, and that whatever advantages the Germans may have acquired have been accomplished by their better industrial organisation, and the better financial support given by their banking institutions and by their Government. This war has given us our awakening. Our industries will be stimulated to organise efficiently as a direct result of this war; but do not let us fall into the common error, prevalent to-day all over the world, that the only thought we need to give is to the attainment of efficiency in mechanical appliances, in chemical knowledge, and in banking arrangements. These must all receive the fullest consideration, and there would only be

one disaster worse than neglect of these essentials, and that would be the neglect of the human element, without proper consideration of which our industries cannot be efficiently carried on.

The Man Behind the Gun.—Every war correspondent tells us that more important than the gun is the man behind the gun; more important than the Dreadnought are the officers and sailors manning the Dreadnought. Neither you nor I need any telling that this is equally true in industries, and as this country has produced the best man to place behind the gun and bayonet, and the best men to staff the Dreadnought, so, equally, this country possesses the best material for staffing laboratory, works, and offices. The chemical industry is not solely and only a question of science and capital. The managers and workmen are of still greater importance, and it is merely a platitude to say so, and yet there has never been any really organised effort to study the mind and characteristics—delicate and intricate—of the human machine. If you were asked what would be the effect of certain acids or alkalis, or temperatures, or pressures, or vacuums, in producing certain results under certain conditions, you would only require to be told the problem, and your pencils would be hurrying over half sheets of note paper, and you could give a definite, exact scientific answer to the problem. But if any of us were asked what would be the effect of certain conditions of employment in industries, I venture to say that we should each of us find it much more difficult to answer such a question from any scientific basis available at the present moment of the human element.

Problem of the Human Machine.—And yet there is no combination of forces or chemicals so delicate and intricate as the mind and body of the human machine, and for this reason—that no two human minds and bodies are alike. You find that "A" is best influenced if handled in one way, "B" if handled in another way, and "C" must be handled entirely differently to either "A" or "B" to get the best results from "C." You will all remember the story of the Englishman, the Irishman, and the Scotsman, and their mental attitude on leaving the train at the terminus, which, if I remember rightly, was somewhat as follows:—The Englishman jumped out and forgot his belongings; the Irishman jumped out with his belongings; and the Scotsman, after picking up his belongings, looked round to see if the others had left anything behind. Now we only know from experience the mental attitudes of our fellow men. We should class Scotsmen as cautious, but we know that all Scotsmen are not cautious. We should class Irishmen as hot-headed, but we all know Irishmen who are as cool and calculating as any Scotsmen; and as to Englishmen, we should probably class them as less cautious and thrifty than the Scotsman, but we all know of Englishmen who excel any Scotsman we ever knew in caution and thrift; and as to Jews, all the Jews that ever I have met have belied every characteristic of meanness and love of money the comic papers have ascribed to them. Such is the variable nature of the problem we have to deal with in handling the human machine. Now, if you are dealing with chemicals, you know exactly how they will act and re-act under given conditions. If we could be equally certain of the effects of various methods of dealing with the human machine, our problem would not be a difficult one.

Different Views of Profit Sharing.—Under these circumstances, it is not surprising that profit sharing in industries has hitherto met with little or no response from employers, and has not proved attractive to employees. The Board of Trade returns show that the average life of profit sharing schemes in the United Kingdom—and I believe similar results have been shown in the United States, France, and Germany—has been under five years. A profit sharing scheme is started with great enthusiasm, and great hopes are expected from it from both employers and employees, but not from the same point of view. The employer is bound to view the scheme in relation to

* Address to the Annual General Meeting of the Members of the Society of Chemical Industry, held at Manchester, July 14th, 1915.

its effect in producing greater efficiency in production, and greater economy of material and care in avoidance of waste. The employee's point of view is that of some immediate increase in prosperity from the point of view of remuneration. Employees have not yet realised that we are all servants of the public, and that the public are the final masters and employers of capital, management, and labour, and that there is no harder taskmaster than the public. Employers know this, and know that a lifelong devotion to the service of the public would not prevent them as, say, chemical manufacturers from being "scrapped," if I may use the term, by the public when a superior process of production of the commodities they manufactured had been discovered and applied by some other chemical manufacturer.

Labour as Debenture-holder.—Under these circumstances it is no wonder that the time-honoured system of wages and salaries remains master of the industrial field; and, in fact, whatever scheme of profit sharing may be adopted, the payment of interest on capital, and the payment of salary and wages to management and labour, must be recognised as the foundation upon which all profit-sharing schemes must rest. But it is the opinion of some of us that the wages system does not go far enough with reference to the human element in business. It places labour and management in the position of debenture-holders on the business; in fact, the law has recognised this, and the payment of salary and wages is made by law the first charge on all industries, and must be paid out of capital in priority to even the security held by the debenture-holder. Now I ask each of you, if you ever heard of help being given by the debenture-holder in the conduct of business? The debenture-holder's attitude and frame of mind is to sit tight, receiving a moderate rate of interest and, as far as possible, absolute security; and it is only when the business is *in extremis* that he steps in and seizes the undertaking and shows some signs of spasmodic life in trying, at any rate, to make the business worth as much as will ensure him the safety of his capital. These efforts, like the action of an atrophied limb under temporary galvanic stimulus, all jerks and convulsions, are of very little use. Now, compare this attitude of the debenture-holder with the attitude of the ordinary shareholder interested in the profits of the undertaking, especially when the ordinary shareholder sits on the board of directors, as is always the case in our best and most successful industries. There you have alertness and that tension of the bow which will ensure a correct aim, and that the arrow will reach its destination somewhere near the bull's-eye. You cannot get the best conditions under any other circumstances than direct personal interest in the results. Commonsense suggests to each of us that if this is the effect on capital when in the position of debenture-holder, similar effects must result on management and labour as debenture-holders, and that if the best results are only obtainable when the directors have a personal interest in the profits of the business, it must be equally true that the best results can only be obtained when management and labour are directly interested in the profits.

Inelasticity of Present Wage System.—In seeking to remedy this condition, we must remember that wages and interest on capital, as a system, have both stood the test of time. They are a convenient and logical system, even if they do not give us finality. At present we know that, whilst there are three distinct methods of payment to capital—namely, a low rate of interest, with all possible security, for capital as debenture-holder; a larger rate of interest, with less security for capital, as preference shareholder; and the remaining profits or losses for capital as ordinary shareholder—there is only one inelastic system for management and labour, namely, salary or wages. The owners of capital have the power of selection of the terms upon which their capital shall be employed, namely, as debentures at a low rate of interest, but with a maximum security; as preference shares, with a higher rate of

interest, and some amount of security and some amount of risk; or as ordinary shares, taking the remainder of the profits with all the risks of the business. Just as it is found in practice that the debenture-holder, and to almost an equal extent the preference shareholder, take little or no interest in the undertaking in which their capital is invested, so it is found that the sole impulse and inspiration for development, growth, and activity in industries, springs from direct interest in the results as represented by the holding of ordinary shares with possible profits or losses. When the board of directors are simultaneously ordinary shareholders, the greatest amount of efficiency, development, and activity can be attained. The very fact that management and labour are often relegated solely to the position of debenture-holder, has reduced the efficiency of management and labour and their interest in the undertaking in which they are engaged to the level of that of debenture-holder, which, as we all know from experience, is, practically, a minus quantity.

Remedy of Co-partnership.—Now, whilst it is not in the power of any debenture holder or preference shareholder to do more than to provide his capital and receive a fixed rate of interest or dividend, it is in the power of management and labour to do much better than to render more or less perfunctory service in exchange for salary or wages. The interest of management and labour can be encouraged and quickened and stimulated to take the keenest interest in the performance of duty and in the wellbeing of the undertaking in which they are employed. The only way logically in which this can be secured, and the only way in which it can with justice be demanded, is by some system of profit-sharing or co-partnership; in other words, to give to management and labour the same interest as that enjoyed by the ordinary shareholder in the success of the undertaking. I am sure we shall all agree in this, but here our first difficulty arises in the uncertainty of the human element. No assurance or guarantee of the rendering of this special interest, efficiency, and alertness can be either asked for or assured from management or labour in exchange for a share of profits or co-partnership certificates.

Founded on Natural Law.—Whatever firm adopts co-partnership must rely upon the operation of certain laws of human nature, which have been found to be as certain in their effect as, say, the law of gravitation or the action of certain chemicals under certain conditions, and must allow a wide margin for exceptions to the rule. Now, one of these universal laws is that of enlightened self-interest, and the other is that all human nature possesses an intrinsic and well ascertained element of goodness, what we often speak of as "decency," and which results in producing a desire to respond to fair, just, and reasonable treatment from the employer. I am certain that whilst there may be exceptions to the possession of this element of fairness and "decency" and desire to respond fully and wholeheartedly on the part of the employee, the principle on the whole mass of employees can be as certainly depended upon as the law of gravitation, and even in the few cases of exception to this law, if a search be made we shall find that there has been something interfering with the operation of the law, just as there can be interference with the operation of some well-established law of chemical reaction. Very often it is from an entirely erroneous impression on the part of the employee, an example of the extraordinary ingenuity of some men in taking invert views of the motives of the employer. The principle of enlightened self-interest requires that we should, every one of us, seek to achieve the best for ourselves by recognising the rights of others, but mere selfishness sees only a narrow, selfish aim and object in every act. I believe myself truly that as civilisation progresses the highest form of selfishness will be the practice of unselfishness, but we have not arrived at that stage yet, and when disappointing results are experienced from the extension of the benefits of co-partnership you may depend upon it that it is not the principles that I have

mentioned as inherent in human nature that have failed us, but that their operation had been interfered with, just as some law of chemistry can be interfered with, and the human machine has been prevented from properly operating by some wrong view which could and ought to be removed.

Employees' Interest in Avoiding Losses.—The employees as a whole who have been placed as co-partners in the position of being interested in the profits of the business they are engaged in do respond with very few exceptions when co-partnership has been in a spirit of fairness extended to them by the employer, notwithstanding that there may be ignoble exceptions. An increased interest in the business is bound to follow from employees who have received co-partnership certificates and who are interested in the rate of dividend paid to the ordinary shareholder. This interest must rest not only on the advantages of profit-sharing, but also on the possibility of loss sharing; in fact the two must be linked together, or no good result can be achieved. Many of the strongest efforts each of us put forward are made to avoid losses. Very often we are called upon to work harder to avoid losses than in the actual production of profits, and under a co-partnership scheme if a business receives a set-back from losses and the rate of dividend is reduced the co-partner employee participates with the ordinary shareholder in these losses, and so this element of loss-sharing becomes just as essential and necessary to a co-partnership arrangement as the element of profit-sharing. The loss-sharing must be just as real to the employee holder of co-partnership profit-sharing certificates as to the holder of ordinary shares in the business. We each of us know for ourselves that when we are glancing through a stock and share list it is only those companies in which we are particularly interested that we are specially diligent in observing the market quotations of, and that the companies in which we are not shareholders either presently or prospectively receive but a very passing notice. This rule must be equally true of the employee. The business in which the employee is engaged for salary or wages only, without any direct interest in the profits, can receive but a very passing interest as to whether the profits are large or small. It is not human nature to have it otherwise. On the other hand, the business in which the employee is engaged, either as manager or workman, on salary or wages, and who is also a co-partner or profit-sharer, will be one to whom the profits are of vital interest.

How Employees can Share Loss.—In adopting any scheme of co-partnership or profit-sharing we must therefore admit as a basis that the employee must receive salary or wages, otherwise he would be unable to live, and we must also recognise that he cannot take the ordinary risks that capital can take. His skill and labour in fact are his capital, but a capital that cannot be stored. It must be used to-day because it has only a value to-day. Cash capital can take risks that management and labour capital cannot take, therefore the loss-sharing that management and labour can take is the loss of profits. We speak of capital as if it were so much money, but we know, each of us, that our capital in any business is represented by certain lithographic scraps of paper called shares or certificates, and that these have been acquired as the result of labour. They represent our labour in past years. If our labour of past years had not acquired what we call these investments, then the benefits to ourselves of that labour would have been lost to us for ever.

System of Co-partnership Certificates.—Why should we not apply this principle to the employee, and give each year in addition to salaries or wages co-partnership certificates, entitling him to a share of profits in the business? I see no difference myself between the shares acquired by money, which money was acquired by labour of brain and body, and the certificates, representing no cash capital, but all the same acquired by labour of brain and muscle, and entitling the holder to a proportion of profits. This

system would meet the difficulty of the employee who has not cash capital to place at risk. It converts into certificates the only capital the employee has—namely, his services—and offers the employee opportunities each succeeding year of converting his services, not only into salary or wages for the maintenance of himself, his wife, and family, but also into an ever-increasing share in the profits of the business. This system is applicable to all undertakings except a very limited few, employing as a rule a very small number of men, and where the employee can render no corresponding service in return, but even in these limited few we often find this same principle has been applied. For instance, there is no occupation that is more personal than that of a barrister, and yet we find that the barrister's clerk by long-established custom receives a percentage on the fees paid to his chief. I very much doubt whether any solicitor or client engaging the services of any barrister considers for one moment who may or may not be the barrister's clerk, yet I am certain the practice of giving a share of the fees to the barrister's clerk would not have survived if it had not been found that in practice it was profitable for a barrister to continue this system, which has been handed down to us from the wisdom of our forefathers. As far as my knowledge of the history of profit-sharing in the past would enable me to form an opinion, I should say that our forefathers did practise profit-sharing with their staff to a much greater extent than the same is practised to-day, and yet in those days the personal touch of the master was much closer with his staff, and his personal knowledge and supervision of his staff was also greater than is possible under twentieth-century conditions of productive enterprise. My contention would be that because of the fact that the larger the industry and the more complex its organisation the less it is possible for the board of directors or the supreme management to know personally of the individual characteristics of the thousands of employees engaged under their direction, that therefore it has become essential that there should be some co-partnership system introduced into our industries.

Applicability of the System to Chemical Industry.—I know of no industry to which this applies with greater force than to the chemical industry. A British chemical industry, founded upon the principles of co-partnership, with employees trained and instructed as to what these co-partnership principles meant, and realising the opportunities co-partnership offered them, would surely possess employees superior to those of competitors in Germany or elsewhere under mere wage and salary conditions. It is more difficult in the chemical industry than in any other industry to assess the services of each member of the staff, whether as inventor, developer of the inventions of others, or organiser, or rank-and-file employee carrying on the routine process of production. We all of us find an increasing difficulty in gauging the results financially of new developments in chemical industries. Some of the greatest disappointments we have each of us had in our businesses have followed upon the greatest prospects of success. It only wants a chemical process to be delayed in the realisation of full success for losses to result instead of profits. Sometimes the smallest and most insignificant means of development have produced the most profitable results and often the most costly experiments have produced nothing but losses. It must and can only be viewed as a whole, and the success of the industry can only be gauged by the success of all its parts. It is an absolute essential to success in the chemical industry that new and costly experiments should be made and for expensive plant to be installed which may afterwards have to be scrapped. It would not produce that spirit of comradeship and feeling of fairness to discriminate in giving a share of profits between the various members of the staff engaged in various departments of these new experimental developments. It is always possible by means of salary to make special recognition to the possessor of special abilities for the solution of difficult problems, yet

the possessor of these superior abilities might fail in the solution of some difficult problem, whilst another, possessing inferior knowledge and inferior ability, might succeed with an entirely different and what might prove a problem easier to bring to a profit-earning successful conclusion. These adjustments of abilities can best be made in salaries, but the broad success of the undertaking, to which the unsuccessful experiment may have equally contributed with the successful experiment because that ground had to be covered—as men have to cover mountains in search for gold, and cannot discover gold without many borings without results—the broad success of the business can only be recognised so far as the employees are concerned on a system of co-partnership, and I cannot help but think that, working on these lines, the whole staff in the chemical industry, as in all other industries, would respond.

Faith in Human Nature.—I have the utmost faith in human nature, and I believe that human nature can be trusted and depended upon nine hundred and ninety-nine times out of a thousand to respond to fair, just, and proper treatment. The old schoolboy love of fairness and justice continues with all of us right through our lives. Often when we are disappointed with effects produced by co-partnership on employees, if we will search a little deeper we shall find that we have overlooked some point or other in our arrangements which has prevented the best results being attained. In other words, to use a chemical parallel, our temperatures may have been wrong or our catalyst may have been poisoned, and not until we discover the right temperature and prevent the poisoning of our catalyst will our system succeed as it should do. Equally so, as we are in the very infancy of the study of co-partnership and profit-sharing with employees, it may be that we have not yet got all of the details correct, without which the transmutation from a lower value to a higher value cannot be achieved.

Rules for Present-day Co-partnership Schemes.—I would like in conclusion to call attention to certain well-defined rules that must be followed in any co-partnership or profit-sharing arrangement under present conditions. Some of these rules will always require to be observed; others I hope as time progresses will not be necessary:—

1. Profit sharing or co-partnership must not degenerate into charity or philanthropy.
2. Its objects must be the increased success of the undertaking, with increased prosperity for all connected with it.
3. It must not place management in the position of servant to labour through liability to criticism and censure.
4. It must ensure to labour freedom from interference of management in the enjoyment of the benefits derived from profit sharing.
5. It must possess greater stability than a mere system of bonus cash payment.
6. Its benefits must be felt by the wives.
7. It must have a distinctly elevating tendency on management and labour, raising them in the social and intellectual scale, and increasing their power for enjoyment and happiness as well as their power of usefulness.
8. Control must remain with those who find the cash capital.

Basis not Philanthropic.—The whole basis of profit sharing or co-partnership cannot be other than enlightened self-interest for both capital and labour. Any other idea would be destructive to the self respect of the employee, and lead to confusion from the point of view of capital. Philanthropy is own sister to charity, and charity is the mother of pauperism. There is no room for philanthropy in business, there is no room for maudlin sentiment; but there is ample room for a better and improved industrial relationship between capital and labour, one in which labour can become, equally with capital, interested in the results of the undertaking.

Certainty of Results.—Wherever this system can be tried, and has been tried, it has always produced the very

best results, from the case of the fisherman, either under sailing boat conditions or steam trawler conditions, whereby the value of the catch has a bearing upon the amount of payment received by each member of the crew, from the cabin boy to the captain, and many other examples which might be named. Even in time of war the introduction of prize money, and rewards of honour for exceptional individual service, have always produced their effect, and it has always been recognised that these systems were of value to the nation. A naval or military system under which the whole of the prize money, or the awards or decorations, went entirely to the officers and none to the rank and file, would be viewed by the whole nation as impossible and grossly unjust; but under modern industrialism we are coming very nearly to such a system as that. The excuse in industrialism is that the recognition of special services can be made in increases in salary, or increases in wages; but we are rapidly approaching a phase in industrialism under which, by collective bargaining, thousands and tens of thousands of men receive an absolutely uniform wage for a uniform number of hours, regardless of the fact that the work rendered by the units is not uniform, and never can be uniform.

Gains of Co-partnership.—Only by a system of co-partnership, or profit sharing, can payment in addition to salary or wages be given. For not only is it true that wages are paid out of the product of labour, but profits must also come out of the product of labour, whether that labour is the brain and managing power of the directors and managers or the skill and labour of the workmen. The gain to the industries of the country by the adoption of co-partnership or profit sharing would not be confined solely to the stimulating of the direct personal interest of the employees. There would be another gain, which would be the release of the directors and high managers to devote more of their time, freed from minor details, to the consideration of larger problems requiring attention and solution. The present salary and wage system may bind in fetters the employee, but it is only another illustration of the truth of the old Egyptian saying:—"The chain that binds the captive holds the captor." By giving a direct personal interest to the employee, less personal supervision will be required from the employer, and the employer will be freed from the fetters that tie him down to close supervision of the employee. Partners are worth more than wage drawers, and when each employee, in proportion to his ability to affect the result, has become interested in the joint product of brain and muscle, we shall then have reached a solid basis for the chemical industry, as for all other industries, and by freeing labour to participate in the products of its own industry, we shall liberate capital and management simultaneously for the enjoyment of a broader, higher, and more useful life.

City and Guilds of London Institute.—The following Diplomas of Associate were awarded by the Council of the Institute, July, 1915:—To Matriculated Third Year Students of the City and Guilds (Engineering) College (A.C.G.I.). In Civil and Mechanical Engineering—B. Ower (Bramwell Medal), R. G. Howard, S. A. Bremner, E. H. J. Stewart, A. S. Joffé, A. G. Smith, H. M. de Wittmann, G. W. Hogan, K. Singh, S. W. Luscher, E. W. Eglin, M. L. Bramson, F. E. Hobley, R. C. Bonnaud, B. E. Bartrum, F. E. Meyer, F. A. Sharp, R. V. Ramalho, H. F. Marles, H. E. Comben, J. Williams, F. A. Pucknell, H. P. Bloxam, C. E. M. de la Nougerède, H. D. Heath. In Electrical Engineering—B. Hague (Siemens Memorial and Henrici Medals), S. W. Messent, C. Jacovou, C. G. Shaw, H. C. Gibson, W. H. Cable, D. Jacovou, F. F. H. Schroeder. To Matriculated Third Year Students of the City and Guilds Technical College, Finsbury (A.C.G.F.C.). In Electrical Engineering—W. J. Jones. In Technical Chemistry—E. C. Chitty, S. F. W. Crundall, A. T. Grisenthwaite, S. P. Kipping, F. L. Sharp, A. W. H. Uffelmann.

NOTICES OF BOOKS.

The Analysis of Non-ferrous Alloys. By FRED IBBOTSON, B.Sc., B.Met., A.R.C.Sc.I., and LESLIE AITCHISON. London, New York, Bombay, Calcutta, and Madras: Longmans, Green, and Co. 1915.

IN this book the methods of analysing non-ferrous alloys, which combine in the highest degree speed and accuracy, and which are most useful for technical purposes and are not of merely scientific interest, are well described. The main outlines of the processes most frequently employed are first discussed, special emphasis being laid upon electrolytic processes the use of which has been very greatly extended lately. Then the common metals are considered individually, the proposed methods being first generally discussed, and then those which are found most satisfactory in practice are fully treated, experimental directions being given for carrying them out. The special methods suitable for various commercial alloys are described separately. The book is designed to meet the needs of students in technical colleges as well as those of the works' chemist, and it is admirably adapted to both purposes.

The Analysis of Dye-stuffs. By ARTHUR G. GREEN, M.Sc., F.R.S., F.I.C. London: Charles Griffin and Co., Ltd. 1915.

THIS book contains complete schemes for the identification of the most important dye-stuffs, worked out chiefly by the author. The methods described may be regarded as the outcome of the author's highly original and successful researches carried out during the last twenty years. They have all been subjected to the most searching and thorough tests, and may be relied upon to give satisfactory and accurate results. The first chapter contains a short *résumé* of the chemistry of the dye-stuffs, which will be of great value to those who are interested in dyeing but whose general chemical knowledge is somewhat limited; the author has made a wise and careful choice of material, and his explanations are clear and to the point. The most familiar dye-stuffs are then classified according to their affinities and methods of application to animal and vegetable fibres, the system of classification being summarised in a tabular statement. The identification of dye-stuffs upon different fibres is then described in detail with comprehensive analytical tables, and the systematic analysis of pigments and lakes is fully treated. A special chapter devoted to the determination of the constituents of the azo dye-stuffs concludes a valuable book which is sure to receive an enthusiastic welcome from dye-works' chemists.

Elementary Studies in Plant Life. By F. E. FRITSCH, D.Sc., F.L.S., and E. J. SALISBURY, D.Sc., F.L.S. London: G. Bell and Sons, Ltd. 1915.

THIS book contains an excellent course of botany for beginners, fully covering the syllabus of the Preliminary and Junior Local Examinations of the Universities of Oxford and Cambridge. The subject is treated rather more widely than in the usual elementary text-book, and the authors have included a somewhat unusual type of experiment, which will undoubtedly add very greatly to the pupil's interest in the study of plants. For example, many simple physiological experiments are described, the measurement of growth, the influence of gravity on the root, experiments illustrating the relation of the plant to the soil, &c. At the end of each chapter suggestions are made for practical work, and lists of material are given for the assistance of the teacher. The subject is treated as far as possible in relation to the seasons, the early chapters being suitable for autumn and winter work. The book can with confidence be highly recommended for the use of the young beginner; it represents a thoroughly scientific

treatment of the subject, giving an accurate and at the same time stimulating and very interesting account of the elements of botany.

The By-products of Coal-gas Manufacture. By K. R. LANGE, Ph.D. Translated from the German by CHAS. SALTER. London: Scott, Greenwood, and Son. 1915.

THIS book opens with a brief description of the methods of purifying coal gas and separating the important by-products, which are then considered in turn in fuller detail. The composition, examination, and uses of coke, retort graphite, and tar are shortly treated, while methods of testing and distilling gas liquor are explained fairly fully. The preparation of ammonia and the treatment of the gas-purifying agents are discussed, and very short chapters on cyanogen sludge, crude ammonium thiocyanate, potassium ferricyanide, and the cyanogen pigments are added. Naturally, continental practice is chiefly described, and the book does not contain anything particularly novel or valuable for English readers. As an introduction to, or a brief summary of, some portions of a standard treatise it might perhaps be of a certain value to technical students.

Overcrowding and Defective Housing in the Rural Districts. By Dr. HARVEY B. RASHORE. New York: John Wiley and Sons, Inc. London: Chapman and Hall, Ltd. 1915.

THIS small book, which could be read through in about an hour, contains a commonsense and practical discussion of the occurrence, causes, and prevention of overcrowding in rural districts. The author appears to write chiefly in the hope of bringing the owner of country property to a right attitude towards the evils of defective housing, and his sound advice and apposite examples may possibly put matters in a different light for some people. Although he is writing of America and for the Americans much of what he says might find application in England, and people who would not attempt to wade through a scientific and detailed dissertation on the subject could readily follow his argument and realise the value of his conclusions.

La Métallographie Microscopique. ("Microscopical Metallography"). By H. LE CHATELIER. Paris: H. Dunod and E. Pinat. 1915.

PROF. Le Chatelier is peculiarly fitted to speak authoritatively upon the development of microscopical metallography, and in this lecture delivered before the old students of the Paris Ecole des Mines he gave an exceedingly interesting account of the subject. Reviewing first the history of the new science he gave a highly appreciative description of the work of Dr. Sorby, whom he alludes to as "the classic type of English savant" who, although independent of fortune owing to his position, did not consider himself to be condemned to idleness by his wealth, but laboured strenuously all his life. The work of Osmond, from whom the lecturer learnt, is also described, and the delicacy of the methods of polishing, &c., worked out by him is described in detail. Finally, the practical utility of metallography in determining chemical constitution, structure, &c., is discussed, and the lecture as a whole gives an excellent review of the beginnings of the new science, showing clearly how it has opened up new horizons in industrial metallurgy, and has already obtained results of great technological importance.

Medical and Sanitary Inspection of Schools of Fourth Class Districts in Pennsylvania. Harrisburg, Pa.: Wm. Stanley Ray.

THE systematic medical inspection of public schools in America was begun fifteen years ago, but the practice was extended to rural schools only comparatively recently. This bulletin will be of considerable interest to medical officers and inspectors in England, as giving a detailed account of the methods adopted in America; it relates only to schools of the fourth class districts; *i.e.*, those including all town-

ships and organised boroughs having a population of less than 5000. The carrying out of the tests and the methods of filling in the report forms are explained, and some very useful general hints are given. The statistics collected show that of the, roughly, 400,000 children examined nearly 73 per cent were defective in some respect, a rather astonishingly high result, but children with bad teeth were tabulated among the defectives. Twenty-five per cent of the children had defective vision. The data of the teachers' follow-up reports are included, and the improvements effected in a large number of cases clearly demonstrate the value of the inspections. The bulletin also contains the questions to be answered in making a return of a 'sanitary survey,' and instructions for answering them correctly.

CORRESPONDENCE.

THE INDUSTRIES OF THE EMPIRE FAIR.

To the Editor of the Chemical News.

SIR,—For the purpose of accommodating a Fair embracing all the industries of the Empire, an exhibition building is about to be erected in London and will be completed by the Spring of 1917. The area of the building will be approximately three times that of the largest exhibition building now existing in London, and will be known as the Palace of Industry.

A Fair of this magnitude being of National importance must not be promoted on the lines of a private enterprise. It is therefore suggested that the profits of the Fair be distributed amongst the firms taking part, in proportion to the space they occupy.

In order to protect the interests of the various trades, an Advisory Council is being formed embracing representatives of the responsible trade associations and societies of the country.

The secretary of the Fair will be glad to receive the name of any association or society that has not already nominated an official to act on the aforesaid Advisory Council.—I am, &c.,

WILLIAM GLASS, Secretary.

Industries of the Empire Fair,
Lincoln House, High Holborn, London, W.C.
July 26, 1915.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clx. No. 25, June 21, 1915.

Researches on the Glucosidification of Glycerin by Glucosidase β (Emulsine).—By Em. Bourquelot, M. Bridel, and A. Aubry.—Glycerin is a trivalent alcohol which possesses two primary alcoholic functions and one secondary alcohol function. Thus, theoretically with the same glucose it could give rise to five different glucosides—two monoglucosides, two diglucosides, and one triglucoside. Van't Hoff and Bayliss, in their researches on the biochemical glucosidification of glycerin, did not attempt to find out whether they had obtained one or more of these glucosides. Seeing that the number of molecules of glycerin was always about four times that of the molecules of glucose it is not probable that the polyglucosides were formed, at any rate in appreciable quantity, but it would be interesting to know whether both the possible monoglucosides were formed, and if so whether a smaller proportion was obtained of the one corresponding to the glucosidification of the secondary alcoholic function. The authors' researches appear to support this view. In their

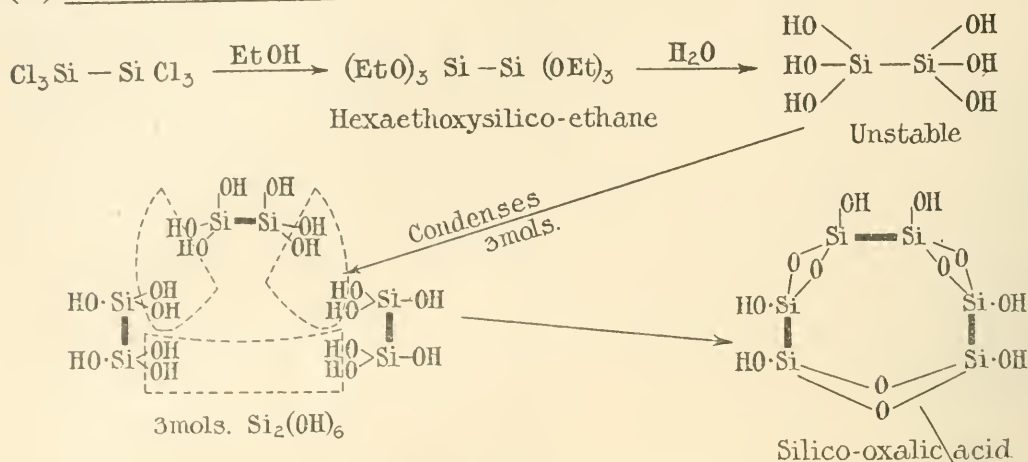
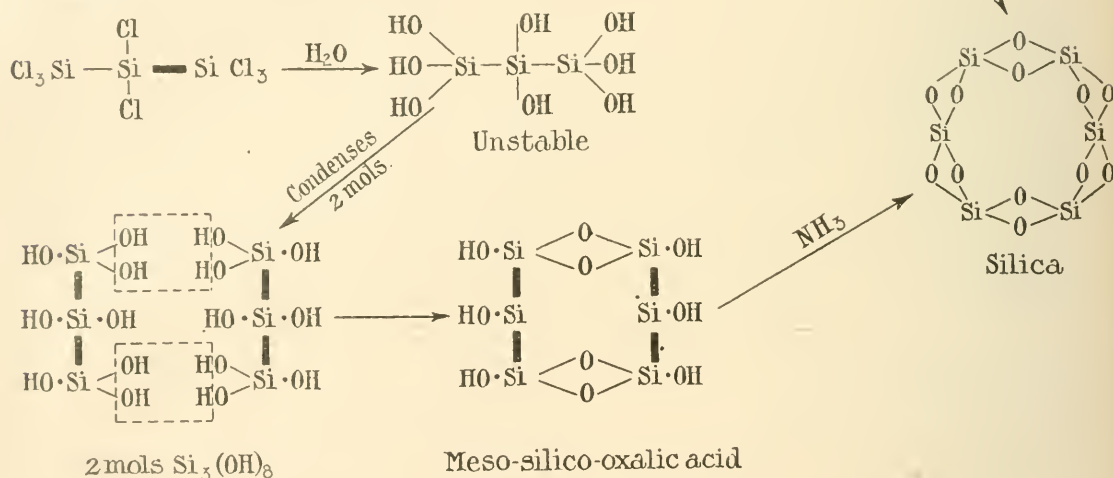
experiments the proportions of glycerin and water to glucose were greater than in the experiments of van't Hoff and of Bayliss. They made two mixtures of glucose (150 grms.), glycerin (800 grms.), emulsine (5 grms.), and water (up to 1000 cc.), and examined them with the polarimeter from time to time. In ten months it was found that the rotation had turned through $16^{\circ} 12'$ to the left. All attempts to make the product of the reaction crystallise were unsuccessful, so it was decided to study it after having dissolved in absolute methyl alcohol and added a little ether to precipitate certain impurities. The evaporation of the ethero-alcoholic solution gave a colourless extract the aqueous solution of which had a rotation of $-27^{\circ} 25'$. The study of its hydrolysis by emulsine showed that the product contained at least two glucosides differing in their rotatory power and in their resistance to the action of emulsine.

MISCELLANEOUS.

Rôle of Science in the Struggle with Germany.

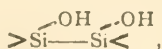
In the *Bulletin* of the "Société d'Encouragement pour l'Industrie Nationale" for March–April, 1915, M. Le Chatelier has published some remarks upon the rôle of science in the struggle with Germany, which are worth the attention of English as well as Frenchmen. He points out that too many manufacturers are apparently limiting their horizon to the establishment of new customs duties, the suppression of the duty on alcohol, and similar schemes, the effect of which must ultimately be to raise the price of articles and lower their quality. He suggests that manufacturers should employ engineers and chemists capable of doing scientific work. Every German factory, however small, has a laboratory in which the process of manufacture is followed and the quality of the products is controlled, and M. Le Chatelier suggests that besides the factory laboratories there might be syndicate laboratories working for all the factories of the same industry, and in certain cases large national laboratories might collaborate with the syndicate laboratories and even with those of the factories in researches of a general nature. This intervention of the laboratory in modern industries, which is one of the causes of the superiority of German industry, entails certain unavoidable obligations, amongst which the first place may be given to the necessity for theoretical and practical laboratory knowledge on the part of the technical directors of the laboratory. Such directors should not be merely business men, as is too often the case, but should possess not only detailed technical and scientific knowledge, but also practical knowledge of laboratory technique. This does not of course mean that they should habitually work in the laboratory, but that they should be capable of doing so. Otherwise they are quite incapable of making proper use of the laboratory, which becomes merely an expensive and useless appendage. The installation of laboratories in French factories, M. Le Chatelier says, would have two very important immediate consequences, the lowering of the price of the product and the possibility of giving the consumer guarantees of quality. One of the most important causes of increase of price is the proportion of waste, which could be greatly reduced by the continuous control of working conditions. M. Le Chatelier concludes that French industries, if they are to succeed in their struggle against German supremacy, must imitate German methods of work. If the direct entry of German goods into France were prohibited they would simply enter through neutral markets. French science has always been ahead of German, and there is no reason why French industry should not take a similar place. But it is absolutely necessary that the heads of the industries should be acquainted with scientific methods, and should be familiar with the practical work of the laboratory.—*Revue Générale des Sciences*, 1915, xxvi. (11).

* Abstract of paper read before the Chemical Society, February 18, 1915.

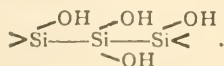
(α) Silico-oxalic acid(b) Meso-silico-oxalic acid

In fact, the above formulæ and name are simply given on account of their entirely imaginary analogy to oxalic acid, and not a particle of real proof has ever been put forward to support this view.

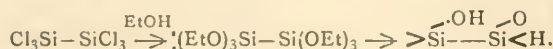
It is quite certain, however, that silico-oxalic acid contains the chain—



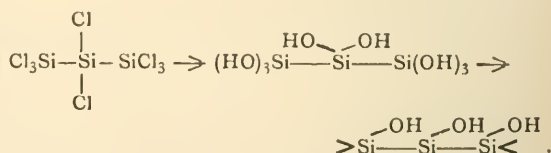
and meso-silicic acid the chain—



The first fact follows from the series of reactions:—



And the second fact follows from the production of meso-silico-oxalic acid from trisilicon octochloride, Si_3Cl_8 :—



Also the volume of hydrogen evolved when these bodies are treated with potash corresponds to these numbers of directly linked silicon atoms. As regards these new formulæ three points call for mention:—

Firstly, the minimum molecular weight given to silica is 6SiO_2 , and it is represented as a cyclic compound. That silica has an atomic weight greater than that represented by SiO_2 is almost certainly correct, because on comparing it with its nearest chemical analogue, CO_2 , of molecular weight 44, we would expect that SiO_2 of molecular weight 60.3 would be a volatile liquid, whereas it melts at over 1600°C . It must be remembered that when we compare CCl_4 with SiCl_4 that both are volatile liquids. There is therefore a fundamental chemical difference in constitution between carbon dioxide and silica, $(\text{SiO}_2)_n$.

The fact that silica crystallises sharply in well defined crystals probably indicates that the molecule has not an extremely high molecular weight. Extremely complex molecules crystallise badly.

Secondly, the tendency of silicon atoms for condensing together in groups of six has frequently been referred to by various authors (*cf.* the formula $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ for feldspar). For example, the writer has recently described some organic silicon compounds of unknown constitution,* and in which very often we obtain one methyl, ethyl, phenyl, benzyl, or naphthyl group to every six silicon atoms (see *Ber.*, 1912, xlv., 2097; 1913, 2442, 3289). The work is still progressing, and W. and D. Asch ("The Silicates," trans. by Searle, London, 1913) has collected together a large number of facts relating to the metallic silicates in a much criticised endeavour to show that the same rule holds throughout the realm of natural silicates.

Thirdly, it is very improbable that the splitting off of water from a substance of formula $(HO)_3Si-Si(OH)_3$ would stop with the production of $O=Si(OH)-Si(OH)_3$, any more than the splitting off of water from ortho-silicic acid,

$HO-Si(OH)_3$, stops with the production of $HO-Si(OH)_2$. The silicic acids condense further, forming complex cyclic silicic acids, whose salts form the metallic silicates.†

Indeed, not a single experimental fact has ever been brought forward to support the view that the splitting off of water from $(HO)_3Si-Si(OH)_3$ would stop with the production of $O=Si(OH)-Si(OH)_3$, and be unattended by any further condensation. On the contrary, all the experimental evidence is against such a view.

2. The second result which follows from the experiments made to isolate synthetic silicic acids of known constitution is this:—

Silicon atoms which are directly united retain OH groups with much greater stability than do silicon atoms which are united through oxygen atoms.

For example, both silico-oxalic acid and meso-silico-oxalic acid will retain all their OH groups *in vacuo* over sulphuric acid at 15° C., and even when dried in the steam oven at 100° C. Whereas silicic acids, such as

$Si(OH)_4$, $O-Si(OH)_2$, $O=Si(OH)-Si(OH)_3$, &c., under the same

conditions part with practically all their OH groups, and become silica. (See, for example, Chatelier, *Comptes Rendus*, 1908, cxlvii., 660; see also Martin, *Trans. Chem. Soc.*, 1915, cvii., 1043).

The following definite rules on this point may now be considered as experimentally established:—

(A). A chain of silicon atoms united through oxygen atoms thus, $-O-Si-O-Si-O-$, cannot have attached

to any single silicon atom even a single OH group which is stably enough united to bear desiccation at 15° C. *in vacuo* over sulphuric acid, or to bear drying at 100° C. in the steam oven. Thus the chain $-O-Si(OH)-Si(OH)-O-$

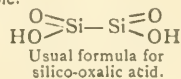
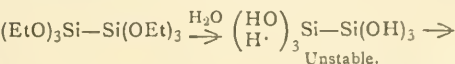
splits off all its OH groups, and becomes $-O-Si<O>-Si-$.

This has considerable practical importance, since it may be stated without hesitation that the almost innumerable published structural formulæ for silicates, in which OH groups as "water of constitution," are represented as directly united to silicon atoms, linked up through oxygen, and capable of bearing comparatively high temperatures, are devoid of all experimental justification, and are founded solely on analytical results, without considering structural probability. The subject is too wide for discussion here, and a further communication will be made.

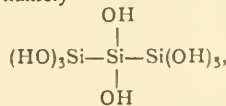
(B). A chain of the two silicon atoms directly united thus, $Si-Si$, can bear attached to each silicon atom at ordinary temperatures *only one OH group*, which will stand desiccation at 15° C. over sulphuric acid, or 100° C. in the steam oven at ordinary pressures. For example, the chain $>Si(OH)-Si(OH)<$ is stable under these conditions, whereas

the chain $-Si(OH)_2-Si(OH)_2-$ will split off water. To give an

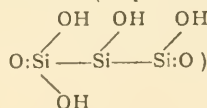
instance, the writer recently showed (see *Trans.*, 1915, cvii., 319) that when hexaethoxysilico-ethane, $Si_2(OEt)_6$, is hydrolysed at ordinary temperatures with excess of water the change proceeds thus, retaining for simplicity's sake the simplest formula for silico-oxalic acid:—



(C). A chain composed of three silicon atoms directly united, thus, $Si-Si-Si$, can bear attached to each outer silicon atom *only one OH group*, while the interior silicon atom can bear *two OH groups*, capable of being retained at ordinary temperatures *in vacuo* over sulphuric acid. Thus the first product of hydrolysis of trisilicon octochloride, Si_3Cl_8 , namely—



is unstable at ordinary temperatures, and splits off water until meso-silico-oxalic acid (simplest empirical formula—



is produced.

These rules are important because we are not longer left to the mere fancy of investigators as regards attributing constitutional formulæ to silicates and other complicated silicon composites, in which chains of silicon atoms, either directly linked or linked up in chains through oxygen atoms. We have now some definite criteria to go upon, and the writer will shortly apply them to elucidating the problem of the constitution of the hydrogen evolving organic silicon compounds, previously described in a former paper.

Birkbeck College, London.

* Some unpublished experiments now in course of completion tend to show that these substances are cyclic compounds, containing directly linked silicon atoms.

† The text-book formulæ given to the silicic acids, viz., $Si(OH)_4$, $O-Si(OH)_2$, &c., are certainly incorrect, inasmuch as such substances do not exist (see the author, *Trans. Chem. Soc.*, 1915, cvii., pp. 1045, 1047, 1048). A substance, such as $Si(OH)_4$, immediately splits off water and condenses to cyclic silicon compounds containing not less than six silicon atoms united alternately through oxygen atoms in the form of a ring. Practically all the metallic silicates are derivatives of such ring compounds, and this explains the innumerable multitude of such compounds. Non-cyclic metallic silicates in all probability do not exist, except, perhaps as a momentary phase of matter at ordinary temperatures. At very high temperatures, however, they probably exist.

American Electrochemical Society.—The twenty-eighth General Meeting will be held in San Francisco on September 16, 17, and 18, 1915. The American Society of Civil Engineers, the American Society of Mechanical Engineers, the American Institute of Electrical Engineers, and the American Institute of Mining Engineers expect to hold their meetings at the same time.

MATTER, MASS, WEIGHT.

SOME FURTHER REMARKS.

By H. STANLEY REDGROVE, B.Sc. (Lond.), F.C.S.

MR. F. H. LORING's further contribution, "Mass, Weight, and Electrical Inertia," published in the *CHEMICAL NEWS* (vol. cxii., p. 37) contains much that will elucidate the subject both for chemists and general readers. However, two or three points still remain to be cleared up. My position is that in his definition of mass and in his description of how it may be measured Mr. Loring has used the term equivocally. But I would make it plain that he by no means stands alone in this: many writers of text-books on chemistry and mechanics—some of considerable eminence—have fallen into the same error, and I am not so much criticising Mr. Loring as endeavouring to expose a fallacy very current in scientific literature. Let me state my point another way. Inertia is defined as that property of a body in virtue of which it continues in a state of uniform rest or motion. Force is required to accelerate (positively or negatively) such a body, and we say that its inertia is measured by the force required to produce a standard acceleration. Now that is the method Mr. Loring gives for measuring mass. Hence, "mass" and "inertia" are synonyms. But "mass" Mr. Loring has defined as "quantity of matter." Hence, either "inertia" and "quantity of matter" are synonyms, or else the fallacy of equivocation has been made. The first alternative, I think, cannot be tolerated. It cannot be squared with the common concept of matter as "extended substance" (for then "quantity of matter" = "volume"), nor with the more philosophical view of matter as the sum of all those phenomena called "properties of matter." Indeed, as I have already said, to make "quantity of matter" mean "inertia" requires "matter" to be defined in a sense totally divorced from the current meanings of that very ambiguous word. To put the whole matter in a nutshell, it is not permissible to define "mass" as "quantity of matter" and then to measure it as "inertia," until it can be proved, for instance, that 2 grms. of oxygen contain twice as much matter as 1 grm. of hydrogen. That the inertia of one is twice that of the other proves nothing save (shall I say?) that the inertia of one is twice that of the other.

Nor is there any justification for making "it a *sine qua non* of matter that its mass (*i.e.*, its inertia) is invariant." Inertia is, in fact, invariant—within the limits of error of observation—for the comparatively small velocities dealt with in elementary mechanics. But the only evidence we have concerning greater velocities (namely, that due to Kaufmann) shows that here inertia is not invariant. The attempt to claim absolute validity for Newtonian mechanics when experiment proves them to have only a limited validity will not do. A system of mechanics possessing absolute validity would be a vastly more complex structure, from which Newtonian mechanics might be deduced by neglecting certain factors of negligible significance over the range of phenomena for which Newtonian principles held good.

Nor can I agree to the distinction between "mechanical" and "electrical inertia," which seems to me to arise from the same fear of casting Newton overboard. Mr. Loring says, "We are not, however, justified in assuming that electrical mass or inertia is the same thing as mechanical mass or inertia." Perhaps we should not be justified in this assumption if inertia were a *thing*; it is not, however, a *thing* but a *phenomenon*, and there is nothing more in a phenomenon than its appearance. We do not so distinguish between electrical, chemical, and mechanical heat, for heat is heat—and inertia is inertia. If Newton's mechanics do not provide for variable inertia, so much the worse for those mechanics; do not let us attempt to bolster them up by mere words, but recognise that their sphere of application is limited.

As to *ratio*, Messrs. Hall and Knight define it as "the

relation which one quantity bears to another of the *same* kind, the comparison being made by considering what multiple, part, or parts, one quantity is of the other," and this definition may be said to be almost classic. Of course, the *number* of units of one quantity may be compared with the *number* of units of some other quantity, for two *numbers* are of the same kind. No doubt this is what Sir J. J. Thomson had in mind when writing, as Mr. Loring says, of "the ratio of mass to weight"; but even the use of it by so great an authority does not justify the expression. For obviously the value of such a "ratio" depends altogether on the units chosen (which is not the case with a true ratio; *i.e.*, the relation between two quantities of the same kind, provided the same unit is used for each), and in Mr. Loring's former paper this ratio is made 1, merely by choosing the units that will make it 1. However, I take it that this point is practically conceded by Mr. Loring, and there is no need to labour it.

Finally, may I point out that I did not in my former article advocate that the term "mass" should be eliminated in favour of "weight," as Mr. Loring's remarks on p. 38 (top of col. 1) seem to suggest. This would be inadmissible because these words have different connotations.* What I did advocate was that "inertia" should always be substituted for "mass." The ambiguity attaching to the former term would thus be obviated, and a great gain in clearness would be effected. The elimination of the expression "quantity of matter," and, indeed, the word "matter" itself, with its undesirable metaphysical associations, might follow as a result. I believe that if Mr. Loring will consider the whole question over again from the beginning, especially in the light of my former criticisms of the doctrine of the indestructibility of matter, references to which I have already given, he will agree with me that this would be an even more beneficial result.

West Ham Technical Institute.

RESEARCH AND CHEMICAL INDUSTRY.†

By Dr. M. O. FORSTER, F.R.S.

So much has appeared recently in the Press, both general and scientific, regarding the bearings of research upon industry, that in addressing an assembly of chemists it is quite superfluous for me to "reconstruct the crime," namely, that whilst holding the priceless initial advantages of early discoverers and unlimited raw products, this country has relinquished, practically without a struggle, a scientific industry of which the educational value far outweighs even the rich material harvest garnered in consequence by another land.

It is not my intention to review the outward circumstances attending this moral and intellectual humiliation. Those circumstances are known in greater or less detail by all present; they have been ably surveyed by Professor W. H. Perkin in his Presidential Address to the Chemical Society (*Transactions*, 1915, cvii., 557), and crushingly epitomised by Professor Percy Frankland in his Address to the Birmingham Section of our own body (*Journal of the Society of Chemical Industry*, 1915, xxxv., 307). I have been requested rather to open a discussion on this painful subject in the hope that others may bring forward views or proposals calculated to assist in removing the stain from our national shield. I welcome the occasion because I am convinced that the opportunity to set our scientific house in order will never recur. I go further, and say that if through our own apathy or that of governments and people this opportunity to bring about a revival of scientific

* It is true that we often say "weight" when we mean "inertia." It would be better, I think, to say what we mean. So far, I am in entire agreement with Mr. Loring's counter suggestion.

† Address to the Annual General Meeting of the Members of the Society of Chemical Industry, held at Manchester, July 15th, 1915.

thought and of its application to social and industrial advancement throughout the Empire, is not seized, nothing can save us from sinking, more or less rapidly, to a secondary position in the class-list of nations. We know the strength of our opponents; do we know our own weakness? This country, in which public opinion is stronger and more healthy than in any other, and in which public opinion has more influence on the life of the nation than in any other, nevertheless has not any public opinion whatsoever on matters relating to higher education or scientific knowledge. In the minds of the great majority of our people the very word "education," in its public as distinct from its personal application, is associated with pathetic squabbles concerning the circumstances in which the education should be given. If all the energy, thought, and genuine—if often misdirected—enthusiasm which have been devoted to this aspect of the subject had been concentrated on the subject itself, how different would be the situation of our people and our country at the present time. Trifling as is the public interest in the real essentials of elementary education, it is vivid and absorbing compared with their appreciation of scientific education, with the result that the pursuit of chemistry has never been held out as a career in the sense that medicine, law, engineering, and commerce are careers. Consequently, the average substantial British parent, whose boy "goes in for chemistry," suffers anxiety regarding his future comparable with that incurred by selecting music, painting, or the legitimate stage.

Hence it comes about that the majority of young men who enter upon chemical studies in this country do so as enthusiasts, with a bias towards the academic aspect of the subject, attracted more by theoretical problems than by the application of chemistry to industry. They have the enthusiasms and faults of hero-worshippers, having been nourished and stimulated by the numerous and wonderful researches which have gone to the construction of modern chemistry. Their three years' course is all too short for the assimilation of the principles of their subject, and at its close they are expected by parents and guardians to be fit to earn their living as chemists. More remarkable still, the manufacturer has sometimes thought that the newly-fledged recruit can improve immediately upon his long-established methods, offers him 35s. a week to try, and is hurt and disappointed when he fails. This brings me to the first joint in our chemical harness. Chemistry is not a "career" as understood by the public from whom chemists should be drawn, and until it is recognised as such, the type of mind which would be anxious to apply chemistry to profitable ends, and is capable of so applying it, will join our ranks by accident alone. Such minds are wanted, badly wanted, in order to organise the research minds, and to co-ordinate their products. This aloofness of the career-seeker is largely due to the stupid confusion which has been allowed to paralyse the career-seeker's parent in the matter of nomenclature. This country is notoriously a label-worshipper, largely in consequence of our intellectual laziness, for label-worshipping saves trouble. Politics, religion, schools, universities, professions—all are accepted by the label which they bear, and it is easily comprehensible, therefore, that the profession which has no label is ignored by the public. Not being legally entitled to call ourselves "chemists," we are driven to such subterfuges as "professional chemist," "works' chemist," "technological chemist," "consulting chemist," "research chemist," "analytical chemist," or even the worse abomination, "scientific chemist." How is a bewildered public which, from childhood to old-age, has perambulated, walked, hobbled, or driven past the "chemist's shop" (5 per diem for seventy years =) 127,750 times, to dissect out these subtleties." In Austria, France, Germany, Italy, Spain, Switzerland, the United States, and other countries, this confusion does not exist, and it is no reflection on pharmacy, a calling which demands careful training and high personal qualities from those who follow it, to say that British chemistry has been

grievously handicapped by the perplexity of the public on this particular point. A rose by any other name would unquestionably smell as sweet, always provided that the geraniol, citronellol, and phenylethyl alcohol were present in the right proportion, but chemists would smell much sweeter in the public nostrils if they did not have to open their intercourse with an explanation.

The next point I desire to make is that the initiative in employing chemists must come from the manufacturer; the converse process is impossible, for the newly-trained chemist or the young demonstrator is obviously debarred from touting for problems, and he cannot therefore thrust himself upon the manufacturer. The latter should have at least a rough idea of the kind of work produced at any particular college, and make a selection of the people who might be useful in dealing with his aspect of the subject. If he is not disposed to employ them on his premises, he could at least provide them with raw material, or with problems which, if successfully handled and solved, would not only help him, but would give the instructors in that college the scent for technical inquiries. This would provide the first requirement in a course of genuine technology, a stimulus, and I am convinced that scores of chemists have been lost to industry from the absence of this connecting link. The young demonstrator, anxious and willing to work at anything useful, would be thrilled and exhilarated by a kilo. of waste material from Messrs. X. and Y.'s manufacturing process, and a request to ascertain whether any valuable constituent was being thrown away; his mind would be directed forthwith into that particular field of industry, and whatever he found, even if it amounted to nothing, he would insensibly become potentially more useful to Messrs. X. and Y., so that if these gentlemen ever did summon up courage to employ a chemist he, or the post-graduate student who had helped him, would be a suitable man to engage. This kind of association between the manufacturer and the college would not take bread from the mouth of the consulting chemist, because Messrs. X. and Y. would probably not have consulted him in any case unless they had been confronted with some unusual dilemma; they certainly would not have thrown away ten good guineas on anything so uninteresting as waste products, because they are only just beginning to realise that the utilisation of such materials will sometimes determine, from the commercial standpoint, the success or failure of a process.

In my belief, this chasm between the college and the factory is responsible for as much mischief as any other circumstance, for, quite apart from the fact that it is bridged in Germany and the United States (for France I cannot speak with first-hand knowledge), the estrangement proceeds in a vicious circle. The factory ignores the college, the demonstrator is not caught young, he therefore grows into an academic professor who, having become deeply interested in theoretical problems and shy of industrial ones, diverts each generation of students more and more away from the factory. The factory responds by despising "pure research," which is a fresh misfortune, because a nibble at research, and the acquisition of those habits of accuracy, responsibility, and inquiry essential to its prosecution, is the minimum qualification with which a diploma-student should be equipped on entering the factory if he may hope to gain a position of maximum utility therein.

Proceeding from this reluctance of the manufacturer to employ chemists excepting when embarrassed by emergencies, there is an enormous loss of potential usefulness in consequence of the following circumstances, which are convincingly demonstrated at Ludwigshafen, Leverkusen, and Hoechst; they apply also to factories employing only fifty chemists, and in lower degree to smaller staffs. Excluding geniuses, the masculine make-up is mentally so ordained that although ample promise may be given at the age of thirty, full development is not usually reached before forty, and in many cases even later. If then a factory staff of fifty chemists recruited at twenty-two or

thereabouts, be allowed to develop under the influence of factory surroundings and requirements, there will prevail throughout the organisation an interchange of thought and outlook contributing to the highest degree of chemical development along the lines of individual temperament. The legal-minded man will gravitate towards the factory patent-office, the book-worm towards the library. The skilful analyst will become the indispensable and time-saving support of the discoverer, who will ransack raw or waste materials assisted by the man who has found his calling to be preparation. The machine-lover will devise new plant for translating grammes into hundredweights, the human person, with less taste for deep study than a desire to knock about, will become a sufficiently trained and agreeably pushing salesman. The whole point is that at twenty-two, one is only dimly conscious of being either legal-minded, a book-worm, an analyst, a discoverer, a preparator, a mechanician, or a human person, and that, given the necessary chemical rudiments, a plunge into the above-sketched system is the best way for a young chemist to classify himself. Then, imperceptibly but surely, out of the fifty there will emerge a Duisberg, or a Berntsen, capable of running the whole team, observing the psychology of the newcomers, adapting them to the departments for which they become clearly suited, and eliminating those who are not destined for any department at all. In a word, the factory becomes a Technological University.

It may be argued that this is a counsel of perfection and beyond the capacity of this country to adopt. If that is so this country must be content to relinquish its position in the world. The age of pioneering in the rough-and-ready manner—that kind of pioneering in which the British national genius is easily first—draws rapidly to a close, and on to this character, which will still have great value, there must be grafted a willingness to study patiently and a capacity for combined effort. In my belief it is foolish, and wickedly foolish, to suggest that the fine chemical industry has been stolen by Germany rather than earned. Foolish because it is not true, and wickedly so because, by pandering to our national vanity and suspicion of learning, it leaves the real seat of the disease untouched. What has really happened is that Germany has recognised more quickly than we have that clearing the ground is only the first step in building a house, and that if we want to build one also we must employ architects and builders. I am endeavouring to emphasise the factors which in my belief are the principal causes of failure in the past, but in doing so it must not be supposed that I hold ourselves blameless. We chemists also are inculpated, although on different grounds. In the past we have not pulled together as we should have done. Faraday entered the service of science imagining that its pursuers became “amiable and liberal,” but his disillusionment remains the disillusionment of many to-day. We are not, I hope and believe, less loyal to one another, less generous-minded, vainer, or more jealous than the general public, but we cannot place ourselves on any lofty pedestal in this respect. Such human failings and occasional deficiencies in a sense of business responsibility have sometimes alienated the sympathy and trust of the business world, and confidence must be restored before the new era can dawn. In the process of national stocktaking which the present terrible discipline has instituted we chemists may learn our lesson too, and realise that co-operation, organisation, and single-minded devotion to the first principle of scientific work—namely, truthful and wise judgment—must henceforth be our only watchwords. In moments of frankness the citation has fallen lately from the lips of many a business man. I make no pretence of escaping it myself, and my fidelity to chemistry and chemists is undiminished, but some one must say these things, and they must be taken to heart, otherwise the present opportunity will be squandered as opportunities have been squandered in the past. My only reason for an unvarnished reference to such points is that, like the rest of the nation, British chemistry is on trial for its life, and it is quite as certain

as any other natural process, like the succession of day and night, that unless we review our own weaknesses and shed them like filthy rags we shall not stand in shining raiment before the judgment-seat of posterity.

On the academic side, for which alone I am in any sense competent to speak, there is certainly room for improvement. In the past we have been victimised by the principle of the hole-and-corner. Appointments to important posts have been sometimes made in the most casual manner, and through the preponderating influence of distinguished and benevolent gentlemen, who have either never been in close touch with the persons and principles involved, or have by passage of years long ceased to be in touch with them. It is all part of our absurd system of assuming that because a citizen has reached a commanding position in one of the recognised careers he is therefore competent to exercise a determining voice in the adjustment of everybody's difficulties, and it arises also from the national intellectual laziness, since it appears to save trouble. But life is becoming much too complicated for the universal genius, and, like all processes which “save trouble” on inverted premisses, it only makes trouble, including England's present difficulties. On this question of appointment to higher posts, for instance, would it not be much more practical if the selection committees as at present constituted were limited in their duties to laying down the conditions, weeding out all but six or eight candidates, and having requested the candidates themselves to select the best of their number, reporting this decision to the superior body, which could still exercise the veto if necessary? This device has obvious advantages, prominent among which is the fact that in a small profession like our own the six surviving candidates for a chair know far more about each other's capabilities and real character than the selection committee are likely to know. Another advantage would be the curtailment of what may be called appointment by clan or school, which sometimes fails to select the best man because he belongs to the less powerful combination, or because he does not belong to any combination at all. It is a lamentable extension of the trust system to patronage, and is based on the totally erroneous hypothesis that any old pupil of the distinguished professor is better than the best of the undistinguished one. But a less obvious, although incalculably more sweeping advantage, would be the cultivation of independence among us from the very outset of our life-work. It is inevitable, and in fact wholly proper, that the young chemist should receive his early employment by patronage in its undegraded meaning, because the patron is usually the only person who knows anything of his possibilities, but he quickly finds that in prevailing circumstances promotion depends quite as much upon avoidance of offence as upon professional achievement, and this discovery may have the most warping and mischievous effect upon all but the most robust characters. No chemist who has intimate knowledge of the system can deny the existence of this evil, and every academic chemist who has reached middle life could in a heart-to-heart conversation give examples of its deplorable results. The same principle applies to selection or non-selection for membership of that august body which, as this is an academic discussion, I will entitle the Imperial Association. Every year two harassed and thoroughly conscientious councillors are subjected to all sorts of well meant influences in favour of the various fifteen or twenty candidates in the subject which they represent. The work of some of these candidates they do not know, or temperamentally cannot fully appreciate, and as decency forbids the public exertion of the well meant influences, these inevitably operate in holes and corners. Candidates, potential or kinetic, know perfectly well of this, and it is humanly impossible for them to escape entirely the effects of their knowledge. The whole system seems to me utterly wrong, and would it not be better in this case, as in the foregoing one, for the candidates themselves to select the fortunate couple from their number, or for the

whole body of chemical members to relieve the two or three councillors of their burdensome responsibility? I am aware that the proposal is revolutionary, but we think rapidly nowadays, and twelve months ago he would have seemed crazy indeed who predicted that within the year Westminster would be innocent of party and Hyde Park undecorated by the purple, green, and white.

Far from being discouraged by the outlook, I believe that British chemistry will gain strength and vitality from its ordeal. There is evidence on more sides than one that the body politic and the people of which governments are made are anxious and willing to render helpful service in the resurrection for which we long, and the final outcome of their repentance is largely in our own hands. Two examples, one commercial the other political, will suffice to illustrate this evidence. In a pamphlet entitled "The Aniline Dye Question," by Mr. Charles Diamond, a member of the Users Committee, among the concluding passages there occurs the following:—"We have shown that as a people, as nations, and as an empire we have not feared to meet the armed might of Germany, but battles won by the sword are hardly more necessary or vital to us than those we must win in the paths of peace. And of our peaceful pursuits, our trade, industry, and commerce are not the least important. This national effort if successful will make for higher and better scientific education, and will promote and develop other important subsidiary enterprises. It will teach us the power and utility and need of combined effort on a large scale, and will assist to break down the isolation, narrowness, jealousy, and all-for-selfness which hamper national progress. Here again there is much to be learnt from the Germans. It will also give us much needed confidence in our ability to still hold our own even in the most difficult circumstances. It will help us to elevate and dignify industry by organising it on a scientific, educational, and intellectual basis. What it would be worth to this country in reputation—as an advertisement, if you like, apart from more tangible and distinctive results—to show the world that the British people have it in them to match their greatest rivals even in their proudest performance!" Some months ago the Royal Society and the Chemical Society presented separate memorials to the Prime Minister setting forth the urgent necessity of taking State action for the purpose of bringing scientific workers into closer co-operation with the leaders of industrial enterprise, at the same time requesting him to receive a deputation. Mr. Asquith empowered his colleagues of the Boards of Trade and Education to receive these deputations from the two Societies, representatives of which accordingly met Mr. Runciman and Mr. Pease, who were supported by the leading permanent officials of the two departments, on May 6, the proceedings being reported in the daily newspapers of May 8. On the following Thursday, May 13, in the House of Commons Mr. Pease announced the intention of the Government to institute forthwith an Advisory Council on Industrial Research, with the object of bringing our universities and technical colleges into closer association with industry, and to bring our industrial leaders into co-operation with skilled workers. The Minister proceeded: "I hope to place on the Estimates for the current year a sum between £25,000 and £30,000, but the demand for money for this purpose will enormously increase as time goes on, and I want to inform the House that whilst we are beginning with this comparatively small sum we think it will develop, and if the scheme is to succeed I believe it must depend upon State help in the years to come, and State help must steadily progress." The political rearrangement which took place during the Whitsuntide recess is no doubt responsible for some little delay in the elaboration of a Government programme, but we cannot at the moment complain that we have pleaded in vain.

To summarise the foregoing remarks, I would say that the first necessity for a closer union between research and industry is the development of a healthy public opinion on

the subject of acquiring knowledge in general, scientific knowledge in particular, and more important than either because it covers both, national wisdom. In order to do this, speaking bluntly, our Governments must advertise scientific methods of business and education by the employment of such methods in their own operations. This is no more undignified than raising an army by advertisement, and after all, what is advertisement but the act of making known, in a word, education itself? In the establishment of such public opinion an important place should be given to the work which chemists do, the part which chemistry has played in the national economy, and the possibilities offered by a wider application of chemistry to industry, in order to attract to our ranks that type of young man which is able to use a chemical training as a weapon for making chemistry pay. Next, although many enlightened manufacturers already make good use of chemistry, their numbers must be increased, and the newcomers must not be too quickly discouraged by what may seem initially an unprofitable investment; one of the ironies of our present position is that a yearly outlay on chemists and a laboratory, moderate even if regarded as a frill or luxury, would often make relatively small inroads into the profits of a concern, whilst regarded as an investment, would be positively gilt-edged compared with many of the enterprises for which the public are invited, frivolously and successfully, to subscribe millions. To quote Mr. Diamond once more, "Bankrupt Turk and Egyptian, American industrial and other wild-cat schemes, South African or other colonial or foreign, land, or financial or commercial, mining or timber enterprises or ventures or swindles, have all got their millions or tens of millions from the British public. Promoters have had enormous profits from hundreds of shaky home flotations, and all this with little or no inquiry or investigation or foresight on the part of capitalists, traders, or other investors." On the other hand it has been recently claimed by Mr. W. J. Dibdin, for many years Chief of the Chemical and Gas Department, Metropolitan Board of Works and London County Council, that "the operations of the Chemical Department of the London County Council and the Metropolitan Board of Works effected a saving in one particular item of £10,000,000 capital expenditure to the ratepayers of London," and he added, "the ratepayers of London have acknowledged the work done by its chemical technologists by abolishing the Department." Such misdirection of effort can only lead to disaster. It is not to be expected that when the war is over there will be any mitigation of Gott strafe British Dyes, Limited, and any other industry which ventures to raise its head, and the situation must be faced with resolute courage and all the resources of our people, both material and intellectual. In the next place, by some process which I cannot clearly foresee, but which must inevitably depend upon sympathetic pharmaceutical agreement, a means must be found by which the respective activities of chemistry and pharmacy may be differentiated in the public mind, so that existing vague ideas on this matter may be clarified. Concurrently with the removal of these moles from the eyes of other people, we must pay attention to the beam or two in our own. If the operation is carried out cheerfully, courageously, and conscientiously, our scientific descendants may have to bless this era as one of chemical regeneration, even if they do curse the ill-wind which waited it to this country.

In conclusion, I venture to lay before the Society as a basis of discussion, the draft of a scheme for a chemical intelligence department which, in my opinion, should be established by Government as a branch of the Board of Trade. Having placed this in the hands of Mr. Runciman and Mr. Pease on May 6th, I have secured the permission of these gentlemen to use it on the present occasion, making it clear, however, that it represents my own personal views, and not the considered opinion of the deputation as a whole. In doing so, I ought to mention that I had not then read the article by Sir William Ramsay which appeared in *Nature* of May 20th, and which covers

a portion of the same ground. Furthermore, it is not contemplated that clauses A (2) and A (3) would conflict with the operations of chemists in consulting practice; on the contrary, under A (5), these clauses should assist in rendering those operations more widely appreciated, recognising, as I gladly do, that the work of such chemists is frequently more entitled to be called "research" than much that is published in the journals of unapplied science.

SUGGESTED SCOPE OF A CHEMICAL INTELLIGENCE DEPARTMENT TO BE INSTITUTED BY H.M. GOVERNMENT AS A BRANCH OF THE BOARD OF TRADE.

A. *Technical.*

1. Classification of chemical discoveries at home and abroad as evidenced by (a) Patent Specifications, (b) Scientific Memoirs.
2. Distribution of chemical information to scientific inquirers and to manufacturers seeking new developments or desiring to improve existing processes.
3. Collection of information regarding the most suitable materials for constructing chemical plant and apparatus on a manufacturing scale, and the most convenient sources for supply of such plant and apparatus.
4. Tabulation of the by-products arising in various chemical industries, and consideration of the most profitable ways of utilising these.
5. Presentations of problems arising out of (3) and (4) to the numerous research chemists throughout the country, such problems to be offered under proper discretionary safeguards and with appropriate remuneration.

B. *Techno-Commercial.*

(By co-operation with the Board of Trade).

1. Classification of foreign chemical products in respect of their distribution throughout the world, with ruling prices, tariffs, cost of transport, and where possible, cost of production.
2. Classification of the resources of the Empire and friendly nations in raw materials, for the purpose of finding novel applications of these.

C. *Techno-Educational.*

(By co-operation with the Board of Education).

1. Classification of data regarding opportunities for chemical instruction and research in various parts of the Empire, and comparison of these with those offered in foreign countries.
2. Consideration of possible improvements and extensions in existing Imperial methods suggested by the information thus gained.
3. Consideration and, where possible, application of methods by which wage-earners of good conduct and adaptability might be trained as technical foremen.

THE STANDARDISATION OF ALKALIMETRIC SOLUTIONS.

By FRANCIS D. DODGE.

THE text-book methods for determining the value of the acid and alkali solutions employed in volumetric analysis are not perfectly satisfactory as regards ease and convenience of manipulation. This will be admitted by most technical chemists, and will no doubt account for the numerous suggestions which have appeared in the chemical literature in recent years, and which have as their object the simplification or improvement of known processes with respect to accuracy as well as convenience.

Any criticism of these methods is not in relation to accuracy of results, because, in general, that is merely a

matter of manipulative skill; but, if one has convenience or economy of time in mind, it would seem that the amount of time and care required is disproportionate, or excessive, as compared with the theoretical simplicity of the end to be attained. Hence, it is presumed that an account of some attempts made towards this very desirable simplification may be not without interest.

All methods so far proposed fall naturally into two classes which can be called direct and indirect. The direct methods involve the use of a standard pure substance, which can be weighed with all desirable accuracy and directly titrated. This appears to be the simplest and most desirable way, provided a thoroughly suitable standard substance can be found.

Of the indirect methods, the following may be noted:—

Physical.

Determination of specific gravity.

Chemical.

Gravimetric determination as BaSO_4 , or AgCl .

Electrolysis of CuSO_4 .

Evaporation with NH_3 , and weighing $(\text{NH}_4)_2\text{SO}_4$.

Distillation of NH_3 , &c.

Iodometric, involving the use of iodic acid and iodates, and thiosulphates.

Sodium oxalate, ignited to carbonate.

All these propositions are lacking in simplicity; under special conditions, some of them may, of course, be useful.

As already indicated, the value of a direct method will depend on the availability of the standard substance. A little consideration will show that the latter should comply as far as possible with the following specifications:—

1. The standard should be easily obtained in a state of sufficient purity.
2. It should be unalterable in the air, at ordinary or moderately high temperatures; i.e., neither hygroscopic nor efflorescent. Hence, hydrated compounds are, in general, undesirable.
3. It should be readily soluble in water and alcohol, thus allowing immediate titration in the cold.
4. It should have a high molecular, or equivalent weight, thus lessening the effect of small errors in weighing.
5. On titration, no interfering product, as carbonic anhydride, should be present.
6. The standard should be free from colour, before and after titration, to avoid interference with indicators.

As far as the writer has been able to ascertain, no standard substance so far suggested answers perfectly these requirements.

Brief consideration and criticism of the degrees of approximation to the ideal exhibited by the compounds already proposed are presented in Table I.

The use of potassium acid tartrate has been strongly recommended by Borntraeger (*Zeit. Anal. Chem.*, xxv., 334), and the writer has obtained excellent results with it. Its purification is not exactly easy, but the main objection is its great insolubility in water and in alcohol, which makes the titration tedious. As an improvement on this, it seemed that an analogous compound might be more convenient as regards solubility, and the acid phthalates appeared worthy of examination.

The acid phthalate of potassium has not apparently been described. It is readily obtained by half-neutralisation of a solution of phthalic anhydride, and crystallises nicely in hexagonal plates.

Acid Potassium Phthalate.

Preparation.—Fifty grms. re-sublimed phthalic anhydride are dissolved in about 200 cc. of water. The solution is exactly neutralised with a solution of about 60 grms. of pure potassium hydroxide in an equal amount of water; 50 grms. more of anhydride are then added, and the heating continued until all crystals are dissolved. The

solution is now made up to about 550 grms. with water, filtered hot, if necessary, and let cool, with continuous agitation to promote the formation of small crystals. When cold, the latter are filtered by suction or centrifuge. The yield is about 125 grms. The product is re-crystallised from 300 cc. of hot water, and dried at 110°.

TABLE I.

Standard substances for acids—	Equivalent weight.	Fails to pass specification No.	
Sodium carbonate ..	53	1	2
Sodium metal ..	23		2
Magnesium metal ..	24	1	2
Borax ..	191		2
Calcium carbonate (Ice-land spar) ..	50		5
For alkalis—			
Oxalic acid, anhydrous	45	1	2
hydrated ..	63	1	2
Acid oxalates ..	—	1	2
Succinic acid ..	59		4
Malonic acid ..	52	1	4
Benzoic acid ..	122		3
Phthalic acid ..	83		3
Phthalic anhydride ..	74		3
Salicylic acid ..	138		3
Nitro and amino acids ..	—	1	
Picric acid ..	212		6
Potassium bichromate ..	146		6
Potassium bitartrate ..	188		3
Betain hydrochloride ..	153.5	1	2(?)

The salt is anhydrous $\text{KHC}_8\text{H}_4\text{O}_4$ with molecular weight 204. It is soluble in 10 to 11 parts of water at ordinary temperatures, and in about 400 parts alcohol.

This compound seems to approximate the ideal substance, as shown by the following facts:—

1. As regards purity, the sublimed anhydride is an admirable raw material and not expensive. Re-crystallisation of the salt is hardly necessary as the impurities derived from the alkali used should be minimal.
2. The salt is stable, anhydrous, not hygroscopic.
3. The solubility in water is sufficient.
4. The molecular weight is higher than that of any compound so far proposed, except picric acid.
5. It behaves like a monobasic acid, and can be titrated with all desirable sharpness.
6. It is colourless.
7. The writer has found it to work well in practice.

The acid phthalate of sodium was obtained by Wislicenus (*Ann.*, ccxlii., 89) as a by-product, and described as glassy, prismatic crystals, containing $2\text{H}_2\text{O}$. Salzer (*Ber.*, xxx., 1496), however, reports that the salt is anhydrous. It is easily prepared in the manner described for the potassium salt, substituting sodium hydroxide or carbonate. In all cases, however, the writer found the fine transparent prisms to contain $\frac{1}{2}\text{H}_2\text{O}$. The salt is soluble in about 9 parts water at 25°, and analysed for moisture as shown in Table II.

TABLE II.

Wt. of salt. Grms.	Treatment.	Time. Hrs.	Loss in weight,	
			Grm.	Percent.
5 (air dry)	Desiccator ..	115	0.0055	0.11
	Heated at 50° C. ..	24	0.0070	0.14
	Heated at 100—110° C. ..	12	0.2410	4.82
1.97 (air-dry)	Heated at 110° C. ..	12	0.0950	4.82
Moisture calculated for $\text{NaHC}_8\text{H}_4\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$				4.57

The salt is thus fairly stable up to 50°; at 100—110° the crystals lose $\frac{1}{2}\text{H}_2\text{O}$ and become opaque, but retain their prismatic form. This anhydrous salt may be used as a standard, but the potassium salt seems preferable.—*Journal of Industrial and Engineering Chemistry*, vii., No. 1.

ON THE PHYSIOLOGICAL ACTIVITY OF COMBINED HYDROCHLORIC ACID.*

By J. H. LONG.

(Concluded from p. 54).

II. The Behaviour of Glutaminic Acid Hydrochloride.

FOR the experiments here I used a pure preparation made in the laboratory by the hydrolysis of casein, and which, by titration of the chlorine and by a nitrogen determination, was known to be practically pure glutaminic acid hydrochloride, $\text{COOH} \cdot \text{CH}_2\text{CH}_2 \cdot \text{CHNH}_2 \cdot \text{COOH} \cdot \text{HCl}$. The salt is readily soluble in water, and 500 mgrms. required 54.5 cc. 0.1 N NaOH for titration with phenolphthalein. This measures the hydrochloric acid and one carboxyl group.

Preliminary experiments showed that solutions of this hydrochloride in presence of pepsin digested egg and fibrin rather rapidly. In the following four trials the coagulum from 1.2 gm. of egg was used in A and B and 5 grms. of prepared fibrin in C and D. In each case 50 mgrms. of pepsin, 600 mgrms. of glutaminic acid hydrochloride, and 50 cc. of water were used. The mixtures were digested at 40° over night. At the end of two hours the disintegration was far advanced, and apparently complete overnight. Blank experiments were made by using killed pepsin to correspond to each case. The mixtures were boiled, filtered, the filters washed, and the filtrates used for nitrogen tests.

TABLE V.

	Total N.	Blank N.	Net N.	Protein.
A	0.1568	0.0358	0.1230	0.7687
B	0.1638	0.0338	0.1300	0.8125
C	0.2471	0.0357	0.2114	1.3212
D	0.2541	0.0357	0.2184	1.3650

The whole of the nitrogen of the pepsin and of the hydrochloride should appear in the blank and should be nearly 50 mgrms., but it is evident that, with the capture of some of the hydrochloric acid by the protein, the glutaminic acid becomes less soluble, and possibly precipitates to some extent. However, the total digestion seems to be from 75 to 80 per cent of what might be theoretically expected, indicating a behaviour much like that of the betain hydrochloride.

A number of digestion experiments were then made exactly as with the betain salt. A solution of glutaminic acid hydrochloride was made containing 6.285 grms. to 250 cc. Five cc. of this contains 125.69 mgrms., or 25 mgrms. of HCl in combination. The N content of 5 cc. is 9.6 mgrms.

As in the former experiments, the coagulum from 1.5 gm. of egg albumin was always taken, corresponding to about 1 gm. of protein. The digesting volume was always 60 cc., of which 30 cc. were made up of a pepsin solution containing 15 mgrms. of pepsin. The digestions were carried on through four hours at 40°, and at the end of this time the mixtures were boiled, diluted, and filtered for the nitrogen tests. The actual digestions began somewhat more slowly than with the betain hydrochloride, and evidently do not go as far. This is probably due to the fact that the hydrogen ion concentrations are lower, as will appear below. Table VI. gives the result of the determinations for soluble nitrogen.

It is seen that these digestion values are not as high as were found in the case of the other hydrochloride, and Table VII. will afford a possible explanation of this. Some of the same solution was employed for determination of the hydrogen concentration at 20°, as described for the experiments with the betain hydrochloride. Table VII. below gives the numerical values.

It is plain that we have in all the dilutions a lower hydrogen concentration than was the case with the betain

* From the *Journal of the American Chemical Society*, xxxvii., No. 5

halt. In the last mixture, equivalent to 150 mgrms. of hydrochloric acid in the 60 cc., the concentration is but little over half that of the corresponding betain hydrochloride. This difference undoubtedly accounts for the lower digesting activity observed in the experiment.

The (H) concentrations observed here are practically all due to the dissociation of the inorganic acid, as the dissociation of the glutaminic acid is very low. The residual concentrations of similar solutions, standing over egg albumin, were found to be very trifling in a number of experiments similar to those carried out for free hydrochloric acid, to be referred to below.

TABLE VI.

	Cc glut. HCl sol.	Total N.	Glut. N.	Net N.	Protein.
A	5	0.0196	0.0096	0.0100	0.0625
B	10	0.0711	0.0192	0.0519	0.3244
C	15	0.1211	0.0288	0.0923	0.5769
D	20	lost	0.0384	—	—
E	25	0.1765	0.0480	0.1285	0.8051
F	30	0.1894	0.0575	0.1319	0.8244

TABLE VII.

	Cc glut. ac. HCl sol.	H ₂ O.	P _H .	C _H .	Theory. C _H .
A	5	55	2.216	0.0060	0.0114
B	10	50	2.010	0.0097	0.0228
C	15	45	1.908	0.0123	0.0343
D	20	40	1.852	0.0140	0.0456
E	25	35	1.811	0.0154	0.0571
F	30	30	1.785	0.0164	0.0686

III. The Behaviour of Protein Hydrochloride.

In the foregoing we have seen the behaviour of hydrochloric acid combined with small groups comparable to the component structures of the protein molecule itself. The acid unites readily with the complex protein, as it does with the amino acid derivatives, and the question of its physiological action here now comes up. In the therapeutic use of hydrochloric acid it is usually administered in the form of diluted solutions of the free acid, and the only important objection to this is the strongly acid taste. To overcome this objection such bodies as the betain hydrochloride have found favour, and it has been shown above that a marked digestive activity is actually present with them. Combinations of proteins and hydrochloric acid have also come into use in recent years, and for these claims of acid strength are made. The experiments to be given below are intended to throw light on this point.

In the investigations I used a form of acid albumin obtained by adding hydrochloric acid to egg albumin and evaporating to dryness at a low temperature. The dry substance was powdered and mixed with enough more albumin powder to bring the HCl content to exactly 5 per cent. The product has a strong acid taste, and is only partly soluble in water. The nitrogen content was found to be 12.25 per cent, but when the product is shaken up in water the amount of nitrogen dissolved is not large. Two experiments illustrate this. Two portions of 2 grms. were shaken up with 100 cc. of water and incubated at 40° through six hours. To one of these portions 50 mgrms. of killed pepsin had been added. At the end of the time the liquids were filtered and on the filtrates nitrogen determinations were made:—

	Total N.	Sol. N.	Pepsin N.	Net N.
A	0.245	0.0196	—	0.0196
B	0.245	0.0209	0.0008	0.0201

While not a large proportion of the protein is soluble, an appreciable amount of the acid dissociates, and may be obtained in the clear filtrate. This is best shown by starting with a larger weight of the powder. Ten grms. were shaken up with 250 cc. of water and allowed to settle

over night. Part of the supernatant liquid was filtered off and portions of 10 cc. were titrated with 0.1 N NaOH.

10 cc. with methyl orange require 1.1 cc.
= 100 mgrms. HCl for whole.
10 cc. with phenolphthalein require 1.7 cc.
= 155 mgrms. HCl for whole.

This result shows that while some of the acid comes through combined with protein, some must be considered as existing in the form of free acid. This amounts to about 20 per cent of the whole acid in the substance shaken up with water.

In the presence of pepsin the mixture undergoes rather a slow digestion, and the amount of hydrochloric acid now found in the filtrate is increased, but not greatly, as the digestion is incomplete. This is shown by Table VIII., where the effect of adding more protein is also brought out. In these experiments 2 grms. of the powder and 50 mgrms. of pepsin were added to 100 cc. of water and digested through six hours at 40°. In some of the cases the coagulum from egg powder with 70 per cent of real protein, and fibrin with 29 per cent of real protein, was added. The results were as follows:—

TABLE VIII.

	Prot. HCl. Grms.	Added pepsin. Mgms.	Added protein. Grms.	Sol. N.	Protein.
A	2	—	—	0.0196	0.1226
B	2	50	—	0.1472	0.9200
C	2	50	1 egg	0.1117	0.6981
D	2	50	2 egg	0.0790	0.4936
E	2	50	2 fibrin	0.1260	0.7875
F	2	50	3 fibrin	0.1142	0.6937
G	2	50	5 fibrin	0.0825	0.5156

The protein in the 2 grms. of the powder used above amounts to about 1.53 grms. Slightly over 60 per cent of this digests when no more protein is present, but the addition of either egg or fibrin brings the digested amount down to a much lower figure. With increasing amounts of added protein the digested fraction progressively diminishes. This is undoubtedly because of the binding of the hydrochloric acid. In similar experiments with other amounts of protein added no greater weight of protein was digested. It appears, therefore, that acid held in this way is not capable of insuring an active digestion, even of its own protein.

The concentration of the dissociated hydrochloric acid is very low in the mixture of the powder with water. This was observed with the mixture made by adding 10 grms. of the powder to water enough to make 250 cc. of solution. The mixture was well shaken through an hour and allowed to stand over night. The acid strength was determined in a cell of the Hamburger type against 0.1 N HCl. The result was found, C_H = 0.00726. The insoluble residue was again shaken with water and allowed to stand. The supernatant liquid gave a lower acid value than before. This operation was repeated twice. The results of the four trials were as follows, showing for the (H) concentrations—

First water, 0.00726; second water, 0.00517; third water, 0.00483; fourth water, 0.00352.

Assuming the hydrochloric acid to be all split off in the first water treatment the concentration should be 0.0548, or with 95 per cent dissociated 0.05296. The amount of free acid available for activation of pepsin is therefore but a fraction of that split off from the betain hydrochloride. A preparation of this character is sold under the name of *oxynin* as a hydrochloric acid substitute.

This holding of the HCl by protein is shown easily in another way, using moist freshly coagulated egg albumin as a substratum. I made a series of experiments in which different amounts of coagulated egg were mixed with 150 cc. of N/15 HCl, and either digested through a certain time or allowed to stand some hours before testing. In

all cases the character of the liquid standing over any remaining albumin was determined. The volume of this liquid which could be filtered off was found. The results of experiments are given in Table IX.

TABLE IX.

	Coagulated from grms. egg.	Treatment.	Volume filtrate (cc.).
A	5	Digested	149
B	6	"	146
C	8	"	138
D	10	"	135
E	5	Not digested	—
F	10	"	—
G	15	Digested	100

In A, B, C, D, and G the digestions were carried through four hours at 50°, with the addition of 50 mgrms. of pepsin. In A and B practically all of the protein went into solution before the end of the period. In C some was left which held a little of the digesting liquid, and in D the amount was still greater. In G the portion digested was apparently very slight, and the volume of liquid which ran through the filter was much less. The weights of actual protein and acid added, expressed in percentages of the protein weight, are as follows:—

TABLE X.

	A.	B.	C.	D.	E.	F.	G.
Weight of protein, grms. . .	3.5	4.2	5.6	7.0	3.5	7.0	10.5
Per cent HCl. . .	10.43	8.69	6.52	5.21	10.43	5.21	3.48

The potential tests in six of the undiluted filtrates, representing the real acid concentration of the supernatant liquids, gave these results:—

TABLE XI.

	A.	C.	D.	E.	F.	G.
P _H . . .	1.696	2.352	2.636	1.403	1.763	2.957
C _H . . .	0.0201	0.0044	0.0023	0.0396	0.0173	0.0011

In A an appreciable amount of free acid is found in the liquid after digestion, while in E, of the same original strength but not digested, the free acid concentration is nearly twice as great. In C there is scarcely enough acid for proper digestion, while in D there was an appreciable amount of albumin left. In G the acid concentration was far too low for digestion, as most of the egg remained undissolved. What passed through the filter was merely acid albumin. In E and F there was, of course, no digestion and very little solution; the amounts of free acid were consequently higher here.

After making the potential tests some of the liquids were returned to the original filtrates and mixed with wash water sufficient to bring all the volumes up to 250 cc. In this way practically everything soluble was washed out of the filters. 25 cc. portions of the filtrates were titrated with 0.1 N alkali and with 0.1 N silver nitrate, after separation of albumin, with the following results:—

TABLE XII.

	NaOH with methyl orange.	NaOH with phenol- phthalein.	NaOH formal titration.	AgNO ₃ titration.	Per cent of HCl recovered.
A	Ca 6 cc.	12.2	14.0	9.7	97
B	Ca 3 cc.	13.0	15.4	9.2	92
C	Trace	12.8	15.5	8.6	86
D	o	13.0	15.4	8.6	86
G	o	5.4	6.5	3.5	35

The results with the methyl orange titration were far from sharp, as is always the case in presence of partly digested protein, and merely give an indication of the practical absence of free hydrochloric acid in three of the cases. Figures showing the results of the formaldehyde titration are also added, but they show no marked increase of protein products in the digestion filtrates. No great importance can be attached to them, for the further reason

that the weak acid concentrations were probably not sufficient to prevent a slight bacterial action between the time of digestion and the titration. But the results of the silver nitrate determinations are interesting. If all the hydrochloric acid had passed into the filtrates the amount of silver nitrate required would have been exactly 10 cc. in each case. But there was always a loss depending on the amount of acid held by the undigested protein. By prolonged washing all of this acid could have been dissociated and washed out. Such acid cannot be considered as mechanically retained, but is doubtless chemically combined. In Sample G two-thirds of the acid is so held, and here the protein residue is very large.

For the actual digestion of protein by pepsin and acid it is not necessary that the amount of free acid should be large, but there must be some excess if the digestion is to be at all rapid. This slight excess may probably come in some cases as a result of dissociation. In Sample C we have about the limit of digestive action, but with the same amount of acid and double the protein there is practically no digestion in G.

These experiments are sufficient to show that combinations of protein and HCl, with not more than 5 or 6 per cent of the latter present, can have no value as digestive agents. This amount of acid is scarcely sufficient to permit the digestion of the protein itself, to say nothing of the digestion of added protein. In this respect the protein acid combinations are not comparable with the combinations with amino acids. In Experiment A, where the digestion is rather rapid and is practically completed in two hours, the (H) concentration was found to be P_H = 1.696. It is interesting to note that this value is between the limits found by Soerensen (*Biochem. Zeit.*, 1909, xxi., 297) for the optimum digestion of egg albumin, as measured by a quite distinct process, viz., the determination of the amount of nitrogen in the digestion filtrate which may not be precipitated by stannous chloride. His optimum is given at P_H = 1.63. It is evident, however, that any marked increase of albumin in A would lead to a decided decrease in the digestive activity.

In these experiments I have received valuable assistance from Miss Mary Hull, to whom my thanks are due.

Resumé.

It has been shown in this paper that the hydrochlorides of betain and glutaminic acid dissociate in aqueous solution to sufficient extent to permit the acid to aid pepsin in the rapid digestion of egg albumin or fibrin. This behaviour is probably typical of amino acid combinations in general. In the case of the betain salt the action is almost equal to that of dilute hydrochloric acid of the same gross concentration. With glutaminic acid hydrochloride the action is somewhat slower, but still marked. In either case, in the mixture of coagulated protein and the hydrochloride, a part of the HCl will leave the latter and become attached to the protein.

Mixtures made by combining hydrochloric acid with protein, in a sense analogous to the hydrochlorides of amino acids, are physiologically much less active. Such mixtures hold scarcely enough acid to digest themselves perfectly. If further amounts of protein are added with pepsin digestion becomes very slow. When the protein and hydrochloric acid are so related as to bring the (H) concentration down to P_H = 2.96 the rate of digestion is slow. This is the case when the weight of the acid is about 3.5 per cent of the weight of the egg albumin and 150 cc. of N/15 acid is the liquid volume.

On the other hand, when the weight of the acid in 150 cc. of N/15 HCl is about 10 per cent of the weight of the albumin, and the hydrogen concentration of the supernatant liquid is about P_H = 1.69, we have very rapid digestion. This appears to be near the maximum of activity. We find all degrees of digestive activity between these limits. Dry preparations of protein and hydrochloric acid about midway between these limits cease to be physiologically active.

WELSH NOTES.

SIR CLIFFORD CORY on July 26 formally opened the new Metallurgical Buildings of the University College of South Wales and Monmouthshire, at Cardiff, which have been erected at a cost of some £3000. For the past seventeen years Prof. Read, the head of the metallurgical department of the University College, has been conducting the work of this important section of education considerably handicapped by want of proper accommodation and appliances. Despite these drawbacks, however, he has achieved valuable results, both in the way of routine education and original research, acquiring for the metallurgical school in Cardiff a position only second to that of the similar institution at Sheffield. Owing, however, to the influx of students from the Treforest School of Mines, who now take the metallurgical course in the study of fuel at the University College, an increased accommodation has become absolutely necessary.

The new buildings consist principally of a series of laboratories, the largest of which is that devoted to assay work. This is fitted with a wind crucible furnace and with all the necessary appliances for assaying. There are laboratories for metallography and for photomicroscopy, the latter with a dark room adjoining. The rest of the buildings include a big balance room, a reading room, a lecture theatre, the professor's private room, and usual offices. An important gift of the Welsh coal owners is that of a large new engine which has been installed in the engineering department for the purpose of conducting efficiency tests.

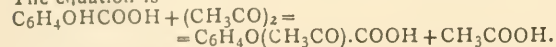
Lord Pontypridd presided at the opening function, and remarked in the course of his address that they were removing the reproach that had been levelled at the backwardness of their technical education, and in future, he thought, there would be little room for complaint. Lengthy speeches were also made by Sir Clifford Cory (in declaring the building open), Principal Griffiths, and Prof. Read.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Bulletin de la Société Chimique de France.

Vol. xvii.-xviii., No. 7, 1915.

Formation of Aspirin.—D. E. Tsakalotos and S. Horsch.—The authors have studied the formation of aspirin (acetyl salicylic acid) from acetic anhydride and salicylic acid as a function of the time and temperature. The equation is—



The products on the left-hand side of the equation when dissolved in water give three molecules of acid (one of salicylic acid and two of acetic acid), while those on the left-hand side give only two (one of acetyl salicylic acid and one of acetic acid). Thus, the transformation is

$3(\text{H}) \rightarrow 2(\text{H})$. In the experiments a weighed quantity (about one molecule) of salicylic acid dissolved in benzene was put into a flask and a given weight of acetic anhydride (about one molecule) added. The variation of the acidity was determined by means of a N/50 solution of barium hydrate, using phenolphthalein as an indicator, 5 cc. of the benzene solution being removed from the flasks at different intervals of time and titrated. The temperatures at which the reaction was studied were 25°, 30°, and 50°. From the results obtained it was found that the velocity of the reaction is that of a reaction of the second order. The temperature coefficient for 10° = 2.2, which agrees with van't Hoff's law, according to which an increase of temperature of 10° increases the velocity of the reaction two to three times. The acceleration of the reaction with the temperature has a limit, for at about 90° the aspirin formed begins to decompose with an appreciable velocity into acetic anhydride and salicylo-salicylic acid.

Nitration of Dimethyl-*m*-phenetidine.—Frédéric Reverdin.—It is often found that aromatic compounds containing one or more ethoxy or ethyl groups behave differently from the analogous compounds containing one or more methoxy or methyl groups. Thus, when diethyl-*p*-aminobenzoic acid or its ethyl ether is nitrated, a mononitro derivative of monoethylamino benzoic acid or its ether is formed, one of the alcoholic radicals united to the nitrogen being eliminated, while in the same circumstances the corresponding dimethyl acid or its methyl ether gives a mononitro derivative in which the two alcoholic residues remain attached to the nitrogen. Similarly, *p*-phenetidine when nitrated behaves differently from *p*-anisidine, the ethyl residue in the dinitro compound of the former being less firmly attached to the oxygen than the methyl group in the corresponding dinitro-*p*-anisidine. The ethyl group of diethylaniline also gives this base characteristics which differ, from the point of view of the reactions it undergoes, from those of dimethylaniline. In order to add to these results the author has studied the nitration of dimethyl-*m*-phenetidine, and will describe the analogous researches on diethyl-*m*-phenetidine in a later report. When nitric acid is added to a cooled mixture of the dimethyl base and acetic acid the temperature hardly rises, and no nitration occurs. If, however, the mixture is heated gently on the water-bath the liquid turns reddish brown, and nitrous vapours begin to be formed at 70°. When the liquid is poured into water a more or less resinous precipitate is formed, which, after some hours, is transformed into yellow flakes. This substance is dinitro-4.6 nitrosomethylamino-3-ethoxy-1-benzene (m. p. 113–114°). If in this nitration instead of heating on the water-bath the product of the reaction is allowed to stand at the ordinary temperature, the liquid gradually turns brown, and on pouring into water a canary-yellow precipitate is obtained. From it the above product of melting-point 113–114° can be separated, and also dinitro-4.6-dimethylamino-3-ethoxy-1-benzene of melting-point 172°. When the nitrosamine derivative (m. p. 113–114°) in solution in acetic anhydride is treated with nitric acid at the temperature of the water-bath the corresponding nitramine (m. p. 137–138°) is obtained. If it is boiled with hydrochloric acid it is transformed into dinitro-4.6-monomethylamino-3-ethoxy-1-benzene. If the nitration of dimethyl-*m*-phenetidine is compared with that of dimethyl-*m*-anisidine it will be seen that the same series of nitrated compounds is obtained, but the reactions begin at a higher temperature.

MISCELLANEOUS.

Institute of Chemistry.—*Past List, June–July (1915) Examinations.*—The results of the examinations of the Institute of Chemistry recently held in London, Glasgow, and Dublin have now been published. Of eleven candidates who presented themselves for the Intermediate Examination, seven passed:—C. E. Corfield; A. Hancock; T. Hopkins, B.Sc. (Lond. and Wales); J. McLeod; J. Ogilvie, B.Sc. (Edin.); Agnes Shore; and A. Stewart, B.Sc. (Glas.). In the Examination in General Chemistry for the Associateship (A.I.C.), E. R. Taylor, A.R.S.M. (Lond.), passed. Of twenty-four candidates who presented themselves for the Final (A.I.C.) Examination, sixteen passed:—In the Branch of Mineral Chemistry—E. Arundel, B.Sc. (Lond.). In the Branch of Organic Chemistry—G. M. Bennett, B.A. (Cantab. and Lond.), B.Sc. (Lond.); A. J. Boyd; R. C. Denington; H. Hepworth, B.Sc. (Lond.); I. Hopper, A.R.C.S.I.; G. L. Hutchison, B.Sc. (Lond.); C. H. Lumsden, B.Sc. (Lond.); J. W. Porter, A.R.C.S.I.; and S. H. Tucker, B.Sc., A.R.C.S. (Lond.). In the Branch of the Chemistry (and Microscopy) of Food and Drugs, Fertilisers and Feeding Stuffs, Soils, and Water—G. A. Bracewell; P. Cheng, B.Sc. (Birm.); A. O. Jones; C. H. Manley, B.A. (Oxon); C. C. Roberts, M.A. (Cantab.); and S. Emsley, B.Sc. (Vict.).

THE CHEMICAL NEWS

VOL. CXII., NO. 2907.

DIFFERENT CHEMICAL ACTIVITY OF FREE AND OF COMBINED WATER.

By HARRY C. JONES and J. E. L. HOLMES.

JONES and Guy (*Publication No. 190, 1912, Carnegie Institution of Washington*) first observed the different physical behaviour of "free" and of "combined" water. The absorption of light by aqueous solutions of such non-hydrated salts as potassium chloride, nitrate, &c., was essentially the same as by an amount of pure water equal to that in the solution. This is what would be expected, since the salt itself has no appreciable absorption in the region of the spectrum investigated, and very little of the water in the solution of the salt in question is combined with the dissolved substance.

We are dealing here with the absorption of light by pure water alone, and this, as is well known, is very pronounced in the region of the longer wave-lengths. The absorption of light by water cannot be satisfactorily photographed, because we have no plate sensitive to these long wave-lengths. A very sensitive radio-micrometer was built for this purpose, and not only the positions of the absorption lines and bands determined by means of it, but what is far more important in the present connection, their intensities.

What we turned to solutions of strongly hydrated salts, such as calcium chloride, magnesium chloride, and the like, very different results were obtained. *Aqueous solutions of these salts absorbed much less light than pure water equal in amount to that contained in the solution.* This showed that "combined water," or "water of hydration," had much less power to absorb light than "free water."

Having found this physical difference between water of hydration in solution and free water, it seemed desirable to see whether there was any chemical difference between "free" and "combined" water which could be detected.

With this idea in mind we undertook the following line of work. We wanted to study a reaction which is effected by water, and in which water itself takes part directly. The saponification of esters seemed to us to be a good example of reactions fulfilling this condition, and we studied the rates of saponification of methyl formate and methyl acetate, first by water alone, then in the presence of aqueous solutions of non-hydrated salts containing the same amount of water as the pure water originally allowed to act on the ester, and finally in the presence of aqueous solutions of strongly hydrated salts containing the same amount of water as the pure water allowed to act on the ester, and therefore the same amount of water as was in the solution of the non-hydrated salt allowed to act on the ester.

The amounts of ester saponified under the different conditions were determined: first time, and concentration being kept constant, and the temperature varied; second, concentration of the salts and temperature being constant, and the time varied; and third, time and temperature being constant, and concentration of the salts varied.

A large amount of work was done to determine the proper base and indicator to be used in titrating the organic acid set free from the ester. It was found that dilute aqueous ammonia was the best base to use, and corallin the best indicator.

As the details of this investigation will soon be recorded in *Publication No. 230 of the Carnegie Institution of Washington*, only a few of the results will be given here to bring out what was found.

In the following tables the percentages of ester saponification are given.

Take first the results where the concentration of the salts and the time were kept constant, and the temperature varied.

TABLE I.—Methyl Acetate.

Salt solutions, normal conc.	15°. 24 hours.	25°. 24 hours.	35°. 24 hours.
H ₂ O	0'076	0'145	0'392
KCl	0'100	0'222	0'722
KNO ₃	0'097	0'196	0'614
NaCl	0'111	0'245	0'806
NaNO ₃	0'105	0'224	0'691
NaBr	0'105	0'227	0'704
KI	0'032	0'036	0'056
NaI	0'077	0'118	0'342
CaCl ₂	0'117	0'385	1'69
MgCl ₂	0'134	0'411	1'67
SrCl ₂	0'128	0'375	1'42
BaCl ₂	0'144	0'377	1'37
Ca(NO ₃) ₂	0'126	0'333	1'34
Mg(NO ₃) ₂	0'125	0'325	1'36
Sn(NO ₃) ₂	0'139	0'293	1'09

TABLE II.—Methyl Formate.

Salt solutions, normal conc.	15°. 4 hours.	25°. 4 hours.
H ₂ O	0'667	3'90
KCl	1'12	7'06
NaBr	1'06	6'98
KI	0'188	2'14
CaCl ₂	2'97	19'84
SrCl ₂	2'56	17'42
BaCl ₂	1'76	13'70
Ca(NO ₃) ₂	1'25	9'84
Mg(NO ₃) ₂	2'54	17'94

In the following tables of results (Tables III. and IV.) the temperature and concentration are kept constant, and the time is varied.

TABLE III.—Methyl Acetate

Salt solutions, normal conc.	25°. 24 hours.	25°. 48 hours.
H ₂ O	0'145	0'289
KCl	0'222	0'513
KNO ₃	0'196	0'431
NaCl	0'245	0'591
NaNO ₃	0'224	0'488
NaBr	0'227	0'517
KI	0'036	0'049
NaI	0'118	0'241
CaCl ₂	0'385	1'05
MgCl ₂	0'411	1'30
SrCl ₂	0'375	0'989
BaCl ₂	0'377	0'965
Ca(NO ₃) ₂	0'333	0'861
Mg(NO ₃) ₂	0'325	0'885
Sr(NO ₃) ₂	0'298	0'713

TABLE IV.—Methyl Formate.

Salt solutions, normal conc.	15°. 4 hours.	15°. 8 hours.
H ₂ O	0'667	2'60
KCl	1'12	4'32
NaBr	1'06	4'26
KI	0'188	1'08
CaCl ₂	2'97	12'76
SrCl ₂	2'56	10'71
BaCl ₂	1'76	7'22
Ca(NO ₃) ₂	1'25	5'24
Mg(NO ₃) ₂	2'54	11'33

In the following tables of data (Tables V. and VI.) temperature and time are kept constant, and the concentration of the solution is varied.

TABLE V.—Methyl Acetate.

Solutions, conc. n.	25°. 24 hours.	Solutions, conc. n/2.	25°. 24 hours.	Solutions, conc. n/4.	25°. 24 hours.
H ₂ O ..	0.145	H ₂ O ..	0.144	H ₂ O ..	0.152
KCl ..	0.222	KCl ..	0.206	KCl ..	0.198
KNO ₃ ..	0.196	KNO ₃ ..	0.201	KNO ₃ ..	0.177
NaCl ..	0.245	NaCl ..	0.242	NaCl ..	0.222
NaNO ₃ ..	0.224	NaNO ₃ ..	0.222	NaNO ₃ ..	0.211
KI ..	0.036	KI ..	0.073	KI ..	0.135
NaI ..	0.118	NaI ..	0.172	NaI ..	0.177
CaCl ₂ ..	0.385	CaCl ₂ ..	0.398	CaCl ₂ ..	0.277
MgCl ₂ ..	0.411	MgCl ₂ ..	0.323	MgCl ₂ ..	0.276
SrCl ₂ ..	0.375	SrCl ₂ ..	0.297	SrCl ₂ ..	0.239
BaCl ₂ ..	0.377	BaCl ₂ ..	0.316	BaCl ₂ ..	0.268
Ca(NO ₃) ₂ ..	0.333	Ca(NO ₃) ₂ ..	0.308	Ca(NO ₃) ₂ ..	0.269
Mg(NO ₃) ₂ ..	0.325	Mg(NO ₃) ₂ ..	0.286	Mg(NO ₃) ₂ ..	0.263
Sr(NO ₃) ₂ ..	0.294	Sr(NO ₃) ₂ ..	0.285	Sr(NO ₃) ₂ ..	0.261

TABLE VI.—Methyl Formate.

Solutions, conc. n.	15°. 4 hours.	Solutions, conc. n/2.	15°. 4 hours.	Solutions, conc. n/4.	15°. 4 hours.
H ₂ O ..	0.667	H ₂ O ..	0.680	H ₂ O ..	0.667
KCl ..	1.12	KCl ..	1.10	KCl ..	1.04
NaBr ..	1.06	NaBr ..	0.988	NaBr ..	0.929
KI ..	0.188	KI ..	0.501	KI ..	0.668
CaCl ₂ ..	2.97	CaCl ₂ ..	2.19	CaCl ₂ ..	1.84
SrCl ₂ ..	2.56	SrCl ₂ ..	1.98	SrCl ₂ ..	1.63
BaCl ₂ ..	1.76	BaCl ₂ ..	1.69	BaCl ₂ ..	1.45
Ca(NO ₃) ₂ ..	1.25	Ca(NO ₃) ₂ ..	1.19	Ca(NO ₃) ₂ ..	1.13
Mg(NO ₃) ₂ ..	2.54	Mg(NO ₃) ₂ ..	2.01	Mg(NO ₃) ₂ ..	1.74

The salts which produce the greatest increase in the velocity of the reaction and which have the largest temperature coefficients are calcium, strontium, barium, and magnesium chlorides, and calcium, strontium, and magnesium nitrates. All of these salts crystallise with water of crystallisation—the amount varying from two to six molecules. These salts, as has been shown in this laboratory (*Publication No. 60*, Carnegie Institution of Washington), are, in aqueous solutions, all strongly hydrated.

With respect to the effect on the velocity of the reaction come next those salts that do not have water of crystallisation and are not appreciably hydrated in solution in water. These are sodium chloride and nitrate and potassium chloride. Some exceptions were noted, but these will be discussed when the results of this work are published in full.

1. The work of Jones and Getman and of Jones and Barrett (*Publication No. 60* of the Carnegie Institution of Washington) showed that the chlorides, nitrates, &c., of such metals as calcium, barium, strontium, and magnesium are very strongly hydrated in aqueous solution. If water of combination or hydration is *more active chemically* than free water, then these salts should increase the velocity of the saponification more rapidly than those salts which are only slightly hydrated, such as those of the alkali metals. From the above results such in fact is seen to be the case.

2. As the concentrations of the salt solutions decrease, the effect on saponification velocity would be decreased much more rapidly in the case of the hydrated than of the non-hydrated salts, since the total amount of combined water would be less in the more dilute solution. Such, again, is seen to be the fact.

3. The work of Jones and Pearce (*Publication No. 180* of the Carnegie Institution of Washington) showed that the hydrating power of a cation is an inverse function of its atomic volume. We should therefore expect magnesium salts to have the greatest effect, then calcium, strontium, and barium. Take the metals with common anions, such as magnesium, calcium, strontium, and barium chlorides or nitrates; the effect is in the order of the decreasing atomic weights of the cations. These conclusions are based upon all the results obtained. In this work we must of course take into account the hydrolysis of the

various salts used. It is true in general that those salts which are the most hydrated in aqueous solutions are the most hydrolysed. This is probably due in part to the greater chemical activity of combined water breaking the molecules of the salt down into free acid and free base.

Taking in account the hydrolysis of the various salts used in this work will not explain the results that were obtained; we therefore conclude tentatively that the difference in action between salts with water of hydration and salts without, on the saponification of esters, is due primarily to the chemical difference between free and combined water.

To account for the greater chemical activity of combined water, we venture the suggestion that combined water is more highly ionised than free water. We hope a little later to be able to test this suggestion.

Johns Hopkins University,
May, 1915.

THE ROCK FORMATIONS OF CENTRAL NEW YORK.

By JOHN A. COGSWELL.

1. *The Salina*.—The Salina is the period of the Onondaga Salt Group, the rocks from which come the salt brines of Central New York. It is quite destitute of fossils, on account of the extreme saltiness of the water during the deposition of the rocks. The crystals of common salt that were embedded in the rocks, long since dissolved out, give the rocks in many places a worm-eaten appearance, and so this is called the "vermicular shale." The specimen analysed was taken at the place where the Chenango Branch of the New York Central Railway crosses the Erie Canal west of Fayetteville. Much of the rock in that locality has the vermicular appearance referred to. It contains a larger percentage of calcium carbonate than was formerly believed to be possible. The results of the analysis are as follows:—

	Per cent.
SiO ₂	5.55
Al ₂ O ₃	3.24
Fe ₂ O ₃	0.90
CaCO ₃	41.45
MgCO ₃	48.57
	99.71

The specific gravity is 2.62.

2.—*The Lower Helderberg*.—Continuing south-eastwardly along the before-mentioned railway to the village of Fayetteville, there are extensive outcroppings of the Lower Helderberg formation in which there are extensive limestone quarries, and the rock is also burned for quicklime. It is one of the great limestone formations, and takes its name from the Helderberg Mountains, south of Albany, the capital of the State. An analysis of a specimen from near Fayetteville resulted as follows:—

	Per cent.
SiO ₂	4.54
Al ₂ O ₃	1.84
Fe ₂ O ₃	0.30
MgCO ₃	12.68
CaCO ₃	80.45
	99.81

The specific gravity is 2.75.

The principal difference between the composition of the Salina and Lower Helderberg is in the amount of magnesium carbonate, the magnesium of the Salina giving way to an increased amount of calcium in the Helderberg.

3. *The Onondaga*.—A few miles farther to the south-east along the railway the village of Manlius is reached, around which are the extensive limestone quarries of the Onondaga division of the Corniferous, one of the greatest limestone formations of the North American Continent. The rock is attractive in appearance, hard, compact, and durable, and furnishes an excellent building material. There are two varieties, locally called the blue and the grey limestone. The rock is utilised in many of the public and private buildings of Syracuse and throughout Central New York. The analysis is as follows:—

	Per cent.
SiO ₂	6.45
Al ₂ O ₃	5.35
Fe ₂ O ₃	0.00
CaCO ₃	78.77
MgCO ₃	8.93
	99.50

The specific gravity is 2.78.

4. *The Marcellus*.—The Marcellus division of the Hamilton period takes its name from a town in Onondaga County, New York, about twelve miles west of Syracuse, on the Auburn branch of the New York Central Railroad. The specimen analysed was taken near Chittenango Creek, between Cazenovia and Chittenango Falls. The outcrop varies in height from five to forty feet. It contains numerous concretions from one to eight inches in diameter; some of the larger in the form of septaria. Most of them are smooth and symmetrical; they are harder and more calcareous than the shales, and remain after the matrix has disintegrated. The shale in many cases bears a singular resemblance to bituminous coal, and much labour and money have been expended in making excavations in the rock for coal deposits. Its principal use is for walks and drives. The older geologists claimed that the dark colour is largely or partly due to the presence of manganese, but our most refined tests failed to reveal even a minute trace. The analysis resulted:—

	Per cent.
SiO ₂	76.89
Al ₂ O ₃	12.80
Fe ₂ O ₃	5.31
CaCO ₃	1.30
MgCO ₃	3.86
	100.16

The specific gravity is 2.69.

5. *The Hamilton*.—The Hamilton take its name from a township and village in the eastern part of Madison County, New York, where there are extensive outcrops. The locality is named from Alexander Hamilton, the distinguished financier and Secretary of the Treasury in Washington's Cabinet. It is a coarse shale. The colour is blue or dark grey on a fresh fracture, but becomes olive or brown on long exposure to the weather. We found no trace of manganese in its composition. The analysis shows that the rocks are clay with a small admixture of limestone. As they decompose they form a fertile soil, on which abundant crops are produced. The railroad tunnel near Cazenovia, New York, on the north shore of Lake Owaghen, presents a good illustration of the Hamilton formation. The tunnel is 1600 feet in length and 17½ feet in height, and extends through the Hamilton division of the period of the same name. Above the tunnel the rock is 28½ feet in thickness, upon which rests 6 feet of soil. The cut through the rock on the eastern end before reaching the tunnel is 630 feet in length, and at the western approach the length is 560 feet. The average height is 40 feet. The rocks on the east end belong exclusively to the Hamilton division, while on the west there is an admixture of Marcellus, which makes these

rocks softer and more inclined to crumble. The specimen for analysis was taken from the tunnel, and the following is the result:—

	Per cent.
SiO ₂	67.79
Al ₂ O ₃	12.26
Fe ₂ O ₃	4.84
CaCO ₃	12.65
MgCO ₃	2.59
	100.13

The specific gravity is 2.65.

A shallow sea deposited the mud, which subsequently hardened and became the solid rock. It is used somewhat as a material for the foundations of buildings.

Our thanks are due to Dr. N. Knight for suggestions in carrying on this work.

Cornell College, U.S.A.,
July 3, 1915.

THE DEVELOPMENT AND CONTROL OF INDUSTRY BY PUBLIC INFLUENCES.*

By HENRY E. ARMSTRONG.

OF late, our chemical industries have been the subject of benevolent criticism, at all hands; it may be that wisdom will ultimately come of the multitude of counsellors, though present appearances serve rather to justify the adage uncomplimentary to a superabundance of cooks. Everybody wants either to do something or see something done—but as nobody knows exactly what to do, everybody wants somebody else to start the ball rolling; the worst sign of all is the constant request for Government intervention. Nobody seems to realise that our urgent need is common-sense, the extent to which we lack courage and enterprise, how greatly the spirit of co-operation is wanting in us—in particular, how destitute we are of the German supervice, the cause of our present plight, power of looking ahead and organising forces—that especially we need to take down the sign "*No expert need apply*" which fills the place of the text-card in too many of our public departments and in the bedrooms of our politicians and administrators, even of the majority of so-called men of business.

Long years ago, Matthew Arnold wrote: "The want of the *Idea of Science*, of systematic knowledge, is the capital want of English education and of English life." Never was statement so true a picture of our state as this is at the present time. The public is so ignorant of the elements of scientific method that, even now, it can scarcely realise that there is such a thing as science, notwithstanding the existence of aeroplanes and submarines and the many ghastly lessons of the war: the Board of Trade would have none of it recently, when dealing with an essentially scientific problem; the War Office still listens to scientific counsel with wadded ears.

The fault is largely in the body scientific: we do not push our own interests sufficiently; I much fear that the one service that will remain unorganised to the end is our own body—the body scientific. Seemingly, we are too hopelessly individualistic to organise ourselves. The Royal Society, which should be the supreme authority in science, declined the task early in the year and it is not likely that those who know us not, our masters the politicians, will seek to bring us together, even for their own ends, as they have no understanding of the use to which we might be put in their service. It is, as Longfellow tells us of "the secret of the sea," only those "that brave its dangers understand its mystery." Indeed, the one chief lesson of

* Address to the Annual General Meeting of the Members of the Society of Chemical Industry, held at Manchester, July 15th, 1915.

this terrible war is the need of bringing home "the idea of science" to the public at large—experts they can never be but some respect for it they can acquire: our clear duty is to persist in urging its infinite value and to insist that it be used regularly and systematically in the service of our country.

All this by way of introduction, just to make obvious my one thesis: *that charity begins at home: that this body needs to wake up and intervene actively in the promotion and protection of chemical industry.* Almost supine hitherto, you have allowed others to tinker with matters which primarily should be your concern.

The chaos is indescribable. The Royal Society has attempted to do something, as much as a body without leaders can be expected to do perhaps, yet what it has done is as nothing compared with what it might do if the spirit of co-operation were evoked in its Fellows. But lessons may be learnt from its partial activity. It appointed three War Committees towards the end of last year; I cannot speak of the Physicists' Committee; the Chemists' Committee, I know, had not been allowed to do anything effective up to a recent date; but the Engineers' Committee, originally a small one, has been enlarged from time to time and, we are assured, has rendered really important service to the Government. Why the difference? Is it not that engineers, like Brutus, are not only honourable, but honoured men, in the sense that they are a professional body, better said perhaps, a body of professionals—accustomed to work together, having learnt that it often pays men to work together? "Union is strength" is their motto. Medical men occupy a similar position; lawyers also: both professions are organised on trade-union lines. But those who rate themselves scientific—the academic party as a whole—are an unorganised rabble, so individualistic, self-centred, and unsympathetic that what is one man's meat is almost necessarily another man's poison. This is both our strength and our weakness—but we shall never win through until we can combine strength with weakness. The lesson of the moment, the lesson a life-time has taught me, is that chemists, too, must become professionals and, like others, sell their services, not give them: we have not yet learnt the lesson of the world, that people only appreciate that which they pay for, that the value of a thing is not appreciated until it has been sold freely. Academic chemists ought not merely to be allowed and encouraged but almost required to work for payment as consultants, like the engineers. The professor pure and simple should disappear. His present rating is too clearly indicated by the action of the American who, when in difficulty how to address the celebrated negro Brooker Washington, feeling that it would not be right merely to dub him *Mister* and unwilling to say *Sir*, as he said, just called him *Professor*!

I am raising a burning question I know. The academic party, the professors, are asking to be consulted on industrial problems, to have their work linked with yours; academic schools are coming into existence, colleges of technology and technical schools, which claim to serve the purposes of industry. But do they? The academic mind is not what you want; the academic mind must be fertilised by contact with practice before it can be of service to you, and the only way is to fertilise it with fees if you wish it to furnish good fruit. Before long this will be the only way of saving the situation; otherwise there will be few purely academic chemists of worth, chiefly because no proper respect is paid to the calling of teacher, because there is too much restriction of the teacher's liberty of action, too much regulation attempted of his activities by those who have no expert understanding of the office, its cares, duties, and responsibilities. No one who has sense and ability will take up a purely academic career, the attraction, the rewards, the opportunities of industry are so much greater, besides which the control of boards of governors and councils will be regarded as insufferable by men of parts.

One main reason why we are so much behind in some of the chemical industries is that the instruction given in our schools has been far too academic in character, in no way in touch with practice. It is all very well for us to speak in their praise in the newspapers, but where are our English chemists? Not yet quite to be reckoned with the proverbial snakes in Ireland, but dangerously few in number. It cannot be said too definitely, either too loudly or too widely, that chemistry has not attracted gentlemen—men of generous mind, good presence, and real ability—in sufficient numbers into its ranks during many years past. We want much of the material that now degenerates into briefless barristers; such material, properly trained, would be of worth and command good pay. Our schools have been overfed with scholarships and scholars have been selected on inadequate tests; too often, indeed almost always, they have been persons of acquisitive power only, destitute of imagination and without breadth of outlook. Examinations like those of the University of London have encouraged the wrong type of man; not a few good men have lost their individuality and failed to develop under the narrowing influence of the course of cramming to which they have been forced to submit. It is to be hoped that the exportation of 1851 scholars abroad will be stopped in future. The depletion of our English schools in the past of their best material has been not the least among the causes which have operated against their development and the consequent lack of men of parts. One public influence which this body should seek to gain over is that of the University of Oxford. I verily believe it to be the greatest in the country. To this end our Society should support the scheme put forward by Prof. Perkin, to make research an integral part of the Honours Degree course, so that men may grow up with a forward outlook and a consuming desire to consider the inner meaning of things and extend the bounds of knowledge. Our schools generally must be favourably influenced if such a measure be passed.

Since the outbreak of war action has been taken in various ways to promote the interests which this body has at heart. First in order comes the Board of Trade Committee, appointed August 25, 1914, with the Lord High Chancellor as Chairman, charged to consider the best means of obtaining supplies of chemicals for the use of British industries. This Committee appointed a Sub-Committee, of which Lord Moulton was Chairman. Apparently the tail soon ran away with the dog. As a result of the report presented by this Sub-Committee a meeting was held of industrial firms, and this was followed by the mysterious appointment of the extraordinary committees which ultimately negotiated the well-known dye scheme, so universally derided within and without Parliament, which this Society allowed to pass into being without one single word of protest.*

The primary mistake was in appointing lawyers to controlling positions on these committees. Such men, however able and eminent, cannot have any real expert feeling on technical problems outside their own professions, and where there is no expert feeling—no proper sense of "technical effect," to use Faraday's expression—there can be no "proportionate judgment" exercised. Parenthetically remarked, it is strange that the technical members of the Committee did not give effect to their objection to the action taken by the Board of Trade by resigning. When Lord Moulton went to Manchester to advocate the scheme on December 8 last year he told his audience that our loss of the coal-tar colour industry was for no other reason than that the English dislike study. He could not have given a more complete proof that he lacked "proportionate judgment"—a more complete failure to understand the real position were impossible. Since Hofmann left us, almost to the present day, English-

* The history of the movement is well told in Prof. Perkin's recent Presidential Address to the Chemical Society (*Chem. Soc. Trans.*, 1915). See also the *Morning Post* of January 20, 23, 24, February 15, 24, 27, March 1, 12, 13, 15.

men—poor devils!—have never been allowed, let alone encouraged, to study in any effective manner either at our public schools or at the ancient universities, and the opportunities have been few elsewhere. During forty years past Oxford has been without a chemical school—how could chemists be trained there? What is far worse, the business community have received no training at our great schools and universities which has in any way helped them to become acquainted with the idea of science. All the ability of the country that the schoolmasters could lay hands on has been forced either along classical lines or, in far fewer cases, into mathematics; the school waifs and strays have usually furnished the material for science. Here has been our surpassing blunder. Not a few of us have shown that we can study, that we do not dislike study; but the enforced studies of the majority, under university influences, have been of unreal things without the mental compass and desires of all but very few; of course, dislike of these has often been apparent. We are simply victims of the literary party, of which the lawyer-politician is the supreme development; he grips us everywhere; until we escape from his clutches and are governed by men of practical instinct who know things and at least hold science in respect, however little they may know of it, we shall make no satisfactory progress.

The academic party in science are first cousins to the lawyer politicians—they too must be made human by the touch of practice, if we are to maintain and develop our scientific and industrial position.

The interests of this Society were touched when the question of Government assistance for industrial research was raised in memorials presented by a recent academic deputation, nominally representing the Royal Society and Chemical Society, to the Presidents of the Board of Trade and Education. (A report appears in the *Journal* of May 15). Besides further expenditure on research, the deputation advocated the formation by Government of a standing committee of chemists to advise manufacturers—but no manufacturer is going either to display his business or bring it under criticism before any academic committee, however appointed. Every manufacturer desires to keep and amplify his secrets, not to disclose them; when a manufacturer wants advice, he will seek out that which is of worth to him and pay for it.

We have to bear in mind that the success of German chemical industry is due to two causes—firstly to the fact that their universities are practical institutions—not collections of competing colleges—properly supported by the State and in touch with the educated community; the idea of science is abroad in Germany, though "science" is not more taught in the schools than it is here; science, however, is respected and has acquired a money value in public eyes, because it has been made real; the company-promoter has been kept in subordination and it has been shown that trust can be placed in those who undertake scientific ventures. In the first place we need not only to put ourselves on a high moral plane but to reform our universities and our university curricula; but reform must come from within to be of use; the office of Government will be to see that the necessary funds are provided: if it interfere beyond this point, as it is seeking to do, it will only do harm. The second and true cause of German success is that the factories are in the hands of experts; moreover and especially, ample provision is made for carrying out all necessary and desirable research work in well-found laboratories within the factories, this being possible because a supply of properly trained men is to be had from the universities. Much is said of the large number of chemists employed in the German works, but it must not be forgotten that the majority act merely as foremen—the Germans having the sense to employ technically trained, expert foremen, whereas we, as a rule, employ uninstructed men who have risen from the ranks, whose ways are too often intensely conservative and obstructive of progress and who can neither take instructions couched in technical terms nor understand the operations they

conduct though they are very skilful in their particular work.

When out in Ceylon last winter, in view of the great importance of the rubber industry and of the small amount which is being spent on research work in connection with it, I made the proposition that Government should levy an "insurance tax" upon all rubber produced in British possessions and require that this be applied to the full scientific study of every particular connected with the industry—the work to be done, however, under the supervision of those concerned in the industry, the task of Government to be merely that of enforcing the application of an adequate sum to scientific inquiry. (*The Times* of Ceylon, November 25, 1914).

Recently, in an introductory address on "The Extension of British Trade," delivered at a conference held at Cardiff at the instance of the City Education Committee, I made a similar suggestion with regard to the coal and iron industries.

(Note.—"For the study of many of the problems connected with coal, I think a tax should be imposed upon the industry and that the proceeds should be devoted entirely to research work, under competent control. I should tax the iron industry in a similar way—at least until it had discovered how to make a cheap rustless iron, an absolute need in countries such as Australia, where artesian bores are of vital importance. I made a similar proposition with regard to the rubber industry recently when in Ceylon. When zinc is 'burnt' in an electric battery, the output of electrical energy is almost theoretical; if we could 'burn' coal effectively, so as to convert the energy stored up in it directly into electricity, we should increase its fuel value to a very great extent; our present methods are extraordinarily wasteful. The problem is one of surpassing difficulty but there is no reason to regard it as insoluble; it is one that we should attempt to solve by serious and systematic inquiry, at public cost. Such matters need to be made the subject of exhaustive inquiry by a competent national commission").

I would extend this proposal to all industries in which the maintenance of research departments is necessary. One part of the tax should be applied to the upkeep of proper works laboratories, another part to the development of research work in places of higher instruction. In cases in which the industry was alive to its own interests and maintained a proper scientific establishment, due allowance would be made and the contribution exacted would only be that required for public purposes in support of technical education. The necessary interlocking of industry and education would at once follow from such a course of action; Government intervention would be reduced to a minimum; and all sensible manufacturers who desired not to go under would make due provision for the scientific control of their industry.

To continue my argument, not only are the Royal and Chemical Societies seeking to advise you but the voice of the excellent President of the Society of Public Analysts has also been heard; moreover, an attempt has been made to establish an Institute of Industry and Science which is to do all sorts of wonderful things by way of bringing science and industry into closer co-operation; it is even provided with a Research Committee, on which figure two chemists, though the rest are mostly persons to whom probably the word research is meaningless. Then there is an Institution of Chemical Technologists which is to put all the different bodies connected with chemistry in their place, to overlord them all; apparently it holds but a poor opinion of this Society, and I am informed that members have joined it because they despair of overcoming your inertia.

And the Institute of Chemistry must not be forgotten. Though this is a body whose constitutional function is no more nor less than that of issuing a certificate of average competency to embryo chemists, it is seeking to acquire merit by thrusting its tentacles into all sorts of quarters where it has no real place. To give it its due, however

in connection with the manufacture of glass and the supply of pure chemicals for laboratory use, it has shown more enterprise and real activity than all the other bodies put together. It is also preparing a comprehensive register of chemists.

The Chemical Society also has recently started a register and has constituted its Council as a consultative and advisory body to deal with all propositions that may be brought forward; I am glad to say, however, that it has the intention of consulting all persons to whom it can refer with advantage.

We are at the moment, in fact, threatened with an overwhelming outbreak of registration fever. Not only the Government but various Societies, from the Royal downwards, are sending out circulars to be filled in: a new form of red-tape-worm disease is upon us—but we want instant action. Germany will not be stayed by any filling-in of forms. It is clear, indeed, that, whilst counsellors and counsel abound, unfortunately there is no evidence of any co-ordinated effort to lighten the darkness—no proper organisation of effort. The result must be chaos. Yet all such agitation is to the good, especially as evidence of desire and determination to set our untidy, ill-furnished, unregulated house in order.

Per contra, in addition to the benevolent influences, well meant if not tending to the development of industry, to which I have referred, others, insidious in character, threatening industrial liberty and to control it adversely, require attention, as showing the need of organisation for defensive as well as for constructive purposes.

The action taken by the Board of Trade in connection with the manufacture of dyestuffs is of this order and cannot be regarded with equanimity, in view of the impassive front that was imposed by the Board of Trade to all suggestions that the scheme must be under scientific control: the complete failure of this Department of Government to appreciate the situation, the entire disregard of the gravity of the issues involved, can only be attributed to blank ignorance; yet it was stated openly in the House that the scheme was Lord Moulton's, who is regarded as a scientific authority in Government circles. The action taken is to be deprecated chiefly on the ground that whatever the present worth of the arrangement as a means of increasing our output of dyestuffs, an invaluable opportunity of developing the industry, even during the war, has been sacrificed and its future establishment arrested if not made impossible. We might so well have served our immediate purpose with greater effect and at the same time have worked with an eye to the future had we sought to develop a complete scientific organisation from the outset. Instead, our Government elected to keep up the card, "no expert need apply," all the time; had this body been alive and alert, no such policy could have been allowed to prevail.

I may now pass to a case of threatened interference with industry in which effective intervention may yet be possible—that afforded by the Report of the Departmental Committee of the Home Office appointed to investigate the danger attendant on the use of paints containing lead in the painting of buildings. The committee was appointed in January 1911 and reported in November 1914, though the report was issued only recently. It is impossible to make the case clear without going into it at length; this I hope to do on a subsequent occasion. Suffice it to say, the committee recommend what amounts practically to the abolition of white lead—an English manufacture—and the substitution of zinc white, which has not hitherto been made here and is not easily made. The committee had not a single scientific man upon it—the only remote approach to one was a medical inspector of factories—and can only be characterised as incompetent to deal either with the issues raised or to appreciate the evidence offered, still less with that which should have been required. It is clear that if legislation affecting industries is to be introduced at the instance of Government departments, the place of science in the attendant

inquiries must be asserted and recognised; it is for this body to act in securing such recognition.

The repressive action of the Local Government Board, attempted probably at the instance of a single official, exercised on several occasions of late in matters requiring the fullest scientific inquiry—in the case of milk and flour, for instance—might also be referred to as further illustration of the need of effective organisation of industrial interests to secure adequate consideration prior to the exercise of control by Government.

I may point out finally that it will be necessary for you, sooner or later and sooner is better than later, to move in the matter of patent laws, to consider to what extent, in future, a specification shall be a disclosure and description of the invention for which protection is sought. The oftentimes arbitrary administration of factory acts on purely red-tape lines, will also call for consideration.

In view of the proved inability of our Government departments to deal with issues which are essentially scientific, to appeal for help, as nominally the Royal and Chemical Societies have done, to those whom we have been forced to describe as flouting science, who hold it in disrespect on account of their entire ignorance of scientific method, is a confession of failure beyond words to describe.

Our plain duty in this Society is to organise ourselves and when we are organised to claim the right to guide Government. But unless the representatives of science subordinate their individualism, sink their differences and form a complete coalition of their forces, no public impression will be made. Much as the public wonder at scientific discoveries—when these are sufficiently sensational and talked about and made obvious—during the last few years, we have done not a little to deprive ourselves of their confidence: company-promoting schemes of the wild-cat order cannot be advanced with impunity—whether guilty or not, we shall all have to do penance on account of not a few of these.

The task before us is indeed colossal. Before the war, Germany had control of the Russian market. It will be long before she will regain this and here will be our opportunity—if our schools take Latin and Greek plays out of their bill and stage Russian instead; and if they add Spanish, we may have some chance in South America also, if meanwhile the Americans do not steal the market against us. The competition we shall have to meet outside Europe, especially in the East, will be greatly intensified, because this will be the chief market open to Germans. I have seen enough recently of German organisation of trade in the East to realise that ours did not compare with it in efficiency.

Unless, however, the desire and impulse come from within, no progress will be made. This country is governed primarily by and from Oxford: if the lessons of the war and public opinion do not cause Oxford to reform, we shall be forced to confess that there is no health left in us and, like the Snark, our industry will "softly and silently vanish away." Some of my friends—*as such* as Sir Ray Lankester—say the University cannot reform; they say the Royal Society cannot reform; they say both bodies must be reformed. Practical men, I am sure, will agree with me that this cannot be true—they will hold with me that no progress will be made unless leaders spring up within such bodies to inspire them with courage, men who will lead them to see how great is the service they can render, how essential that service is to the community.

The development of German industrial chemistry has been from within, as I have said, though it has received great assistance from public sources. The academic party in Germany has done its work thoroughly and honestly and under conditions which have made sound work possible—under conditions of freedom, of *Lehrfreiheit* and *Lernfreiheit*. Such has not been the case here—the Oxford tradition, that it is necessary to be well-read and play games in the afternoon has dominated the situation; it has not been held that it is necessary to be well practised.

The examination fiend has come in to complete our ruin, together with a system of rewards altogether disproportionate, unnecessary and undesirable. German universities have prospered and have rendered the greatest possible service to industry without the assistance of the Honours degree with its attendant classes, also without Fellowships. The German academic party has received full recognition at the hands of the industrial party because, on the average, its products have been found to be of worth: here this has not been the case.

Government cannot help us in these matters. The industrial party will consider the academic party and consult it when the latter can do for industry what the German academic party has done for industry. The Oxford degree in chemistry has been worthless for practical purposes, because men could not get the necessary training, as there was no proper atmosphere in the university; but the tone of the university towards science must be changed entirely if the school that is being started is to be a success. New laboratories alone will not give what is required.

The conditions at Cambridge have been better but not satisfactory and even now far too much is attempted, the time spent in study being insufficient to give the student a practical professional outlook. In the schools dominated by the London University, the student has not been placed in a position to learn, but has been forced to cram and during so long a period that he has suffered severely from mental atrophy and has been spoilt for practice; in few cases has the attempt been made anywhere in our country to give him that forward outlook and the desire to do something himself which is to some extent acquired by every recipient of the Ph.D. degree in Germany.

To progress, we must acquire the desire to do something before we take to learning: knowledge is not power unless it be associated with the desire and power to use it.

It rests with the Royal Society, in my opinion, to give the impulse and start reform, by reforming itself, waking up from its academic slumbers and playing the active part that it is possible for it to play if it only realise what it can do as a live institution. It is our scientific House of Peers; it is not only representative of all branches of experimental and observational science but industrial science has its place in our ranks, although it is to be confessed that we are ultra-academic at present and need a far larger leaven of men accustomed to apply science to practice.

In consequence of the development of the special societies, the Royal Society is no longer of consequence as a scientific society, in the ordinary sense. Unless the forces at its disposal are used effectively, it will cease to be of service and there will be little satisfaction in belonging to it. The Fellows will fail in their duty to the Empire, unless the Society grasp the power which is potential in its hands and claim to be supreme as a deliberative and advisory authority in the interests of science. The voices of scientific workers in our country should be heard as that of one man, through the Royal Society—we should then count for something in the National Councils; it should co-ordinate our scientific forces and link them up with our educational as well as with our industrial system—we should then play our due part in the State and the idea of science would soon be abroad. But to this end, the Society must be organised as a democracy; at present, it is little short of entirely in the hands of a ring of all but permanent, autocratic officials and the Fellows have but little part in its proceedings, as the Council in no way represents the desires and ideas of the Fellows.

The way before us is clear—we have but to group ourselves in sections mainly according to subjects: for example, all the chemists in one section, the physicists in another, the biologists including medical men in a third; hybrid sections might also be constituted, for example, one to deal with education. The policy of secrecy that

prevails in the Society is merely the outcome of an attempt to retain the power in the hands of cliques, in no way worthy of the body or compatible with the proper exercise of its high office.

I claim for this Society a similar position with regard to chemical industry and consider that your influence should be made operative in the highest quarters both directly and through your proper representation in the Royal Society. You have in no way done your duty to yourselves hitherto or rated your office and opportunities, the calls for your service, sufficiently high.

It rests with the younger men among you now to come forward and make yourselves effective as organisers. Organise your forces and use them constructively forthwith you must—the call upon you is imperative; let loose your ideas; many, I know, are afraid to speak: have courage—without it you cannot achieve victory!

MELTING-POINTS OF CHEMICAL ELEMENTS, AND OTHER STANDARD TEMPERATURES.*

By S. W. STRATTON.

THIS table of melting-points of the chemical elements is issued in answer to numerous requests for this information.

The values of the melting-points used by the Bureau of Standards as standard temperatures for the calibration of thermometers and pyrometers are indicated in capitals. The other values have been assigned after a careful survey of all the available data.

As nearly as may be, all values, in particular the standard points, have been reduced to a common scale, the thermodynamic scale. For high temperatures, and for use with optical pyrometers, this scale is satisfied very exactly by taking $c_2 = 14500$ in the formula for Wien's law (see Circular 7, or Scientific Paper No. 11, U.S. Bureau of Standards) connecting I , monochromatic luminous intensity of wave-length λ , and T , absolute temperature: $\log I_1/I_2 = c_2/\lambda \log e (1/T_1 - 1/T_2)$. For all purposes, except the most accurate investigations, the thermodynamic scale is identical with any of the gas scales.

Melting-points of the Chemical Elements.

Element.	C.	F.
Helium	< -271	< -456
Hydrogen	-259	-434
Neon	-253?	-423
Fluorine	-223	-369
Oxygen	-218	-360
Nitrogen	-210	-346
Argon	-188	-306
Krypton	-169	-272
Xenon	-140	-220
Chlorine	-101.5	-150.7
MERCURY	-38.9	-38.0
Bromine	-7.3	+18.9
Cæsium	+26	79
Gallium	30	86
Rubidium	38	100
Phosphorus	44	111.2
Potassium	62.3	144
Sodium	97.5	207.5
Iodine	113.5	236.3
Sulphur	{ S _I 112.8 S _{II} 119.2 S _{III} 106.8	{ 235.0 246.6 224.2
Indium	155	311
Lithium	186	367
Selenium	217 220	422-428
Tin	231.9	449.4
Bismuth	271	520
Thallium	302	576

* Circular No. 35, 2nd Edition, 1915, U.S. Bureau of Standards.

Other Standard Temperatures.

Substance.	Phenomenon.	C.	F.	Variation with pressure (pressure in mm. of Hg).
OXYGEN.. ..	Boiling	-183.0	-297.4	C° = -183.0 + 0.01258 (p-760) -0.0000079 (p-760) ²
CARBON DIOXIDE ..	Sublimation in inert liquid	-78.5	-109.3	C° = -78.5 + 0.017 (p-760)
SODIUM SULPHATE, Na ₂ SO ₄ + 10H ₂ O	Transformation into anhydrous salt	32.384	90.291	C° = 100 + 0.03670 (p-760) -0.00002046 (p-760) ²
WATER	Boiling	100	212	C° = 217.96 + 0.058 (p-760) C° = 305.9 + 0.063 (p-760) C° = 444.6 + 0.0908 (p-760) -0.000047 (p-760) ²
NAPHTHALENE ..	Boiling	217.96	423.73	
BENZOPHENONE ..	Boiling	305.9	582.6	
SULPHUR	Boiling	444.6	832.3	
Ag ₃ Cu ₂	Eutectic freezing	779	1434	
SODIUM CHLORIDE.	Freezing	801	1472	

Melting-points of the Chemical Elements (continued).

Element.	C.	F.
CADMIUM	320.9	609.6
LEAD	327.4	621.3
ZINC	419.4	786.9
TELLURIUM	452	846
ANTIMONY	630.0	1166
CERIUM	640	1184
MAGNESIUM	651	1204
ALUMINIUM	658.7	1217.7
RADIUM	700	1292
CALCIUM	810	1490
LANTHANUM	810?	1490
STRONTIUM	>Ca < Ba?	—
NEODYMIUM	840?	1544
ARSENIC	850?	1562
BARIUM	850	1562
PRASEODYMIUM	940?	1724
GERMANIUM	958	1756
SILVER	960.5	1761
GOLD	1063.0	1945.5
COPPER	1083.0	1981.5
MANGANESE	1260	2300
SAMARIUM	1300-1400	2370-2550
BERYLLIUM (glucinum)	1350?	2462
SCANDIUM	?	—
SILICON	1420	2588
NICKEL	1452	2646
COBALT	1480	2696
YTTRIUM	1490	2714
CHROMIUM	1520	2768
IRON	1530	2786
PALLADIUM	1549	2820
ZIRCONIUM	1700?	3090
COLUMBIUM (niobium)	1700?	3090
THORIUM	>1700 < Pt	>3090 < Pt
VANADIUM	1720	3128
PLATINUM	1755	3191
YTTERBIUM	?	—
TITANIUM	1800	3272
URANIUM	<1850	<3362
RHODIUM	1950	3542
BORON	2200-2500?	4000-4500
IRIDIUM	2350?	4262
RUTHENIUM	2450?	4442
MOLYBDENUM	2500?	4500
OSMIUM	2700?	4900
TANTALUM	2850	5160
TUNGSTEN	3000	5430
CARBON (a)	>3600	>6500

(a) For p = 1 At.

At high temperatures some of the values are quite uncertain; thus, while the melting-point of platinum may be considered accurately known to 5° C. that of tungsten is uncertain by 100° C. or more. Temperatures centigrade are rounded off, and the exact Fahrenheit equivalents are usually given.

COMPARISON OF A FEW METHODS FOR TOTAL PHOSPHORIC ACID IN SUPERPHOSPHATE.*

By C. A. PETERS.

A COMPARISON of several methods for the determination of total phosphoric acid in superphosphate has been made, emphasising the interference of silica in the gravimetric method, and showing that shorter methods give as accurate results as the customary double precipitation as phosphomolybdate and ammonium magnesium phosphate. Nothing new is claimed for the work.

The superphosphate used was home made from ground rock. All but about three quarters of 1 per cent of the phosphoric acid was water-soluble. Aqua regia was used to dissolve the phosphoric acid.

For the determination of the phosphoric acid various procedures were carried out, as follows:—

A.—The official method (*Bull. cvii.*, 2).

B.—The official method, modified by evaporating the liquid on a water-bath, taking up with dilute nitric acid, and filtering through paper to remove silica before precipitation.

C.—Direct weighing of the yellow precipitate as outlined by Baxter (*Am. Chem. Journ.*, 1902, xxxix., 298).

D.—The volumetric process of Pemberton as described by Wiley ("Principles and Practice of Agricultural Chemistry," 1908, ii., 160).

E.—The direct precipitation of ammonium magnesium phosphate in the presence of ammonium citrate (*Ibid.*, 1908, ii., 88).

F.—Same as E, substituting citric acid for ammonium citrate (*Ibid.*, 1908, ii., 98).

None of these methods require description. However, the apparatus used for heating the yellow precipitate to 290–300°, as outlined by Baxter, will be described. This consisted of two six-inch iron dishes, deep form, such as are used for sand baths. The edges of one dish were cut back three-quarters of an inch every half-inch, and bent in so as to make a cover for the uncut dish. A hole in the top of the cover held a cork and thermometer. Triangles inside were arranged to hold two or three crucibles, each covered with a small watch-glass. An asbestos jacket, consisting of a side and top, prevented the radiation of heat. The whole was heated with a Bunsen burner, the flame being protected from draught by an iron conical shield eight inches high.

The results obtained by the different methods are given in Table I., each determination made being listed.

From the comparison of the results given under A and B in Table I. it would be inferred that there was 0.26 per cent of silica in the pyrophosphate when the solution of total phosphoric acid before precipitation with molybdate was not evaporated to dryness. The results indicated

* Taken from a Thesis by Arthur G. Weigell, optionally presented for the degree of B.S. at the Massachusetts Agricultural College at Amherst. From the *Journal of Industrial and Engineering Chemistry*, vii., No. 1.

under C, D, and E, which were obtained by direct weighing of the yellow precipitate by the volumetric method and by precipitation in ammonium citrate, are on the average of 0.17 per cent less than those listed under B. If the results obtained under B (silica free) are taken as standard, then it is apparent that either of three more rapid methods (C, D, or E) give as accurate results as the official gravimetric method. No attempt was made to find silica in any of the precipitates, as its presence is generally acknowledged (Wiley, *loc. cit.*, 78). The results given under C₁ show the decomposition of ammonium molybdate by temperature over 300° and the resulting negative error.

TABLE I.—Total Phosphoric Acid in Superphosphate.

Method.	Duplicates, per cent.		Average per cent.	Variation from B. per cent.
A. Official method	15.30	15.25	15.28	+0.26 (a)
B. Official method (modified) ..	15.07	14.97	15.02	0.00 (b)
C. Direct weight of yellow ppt. ..	14.81	14.81		
..	14.82	14.85	14.82	-0.20 (c)
C ₁ . Same as C, but overheated ..	14.53	14.54	14.54	-0.48 (c)
D. Volumetric ..	14.80	14.86	14.83	-0.19 (d)
E. Precipitated as NH ₄ MgPO ₄ ..	14.85	14.94		
..	14.85	14.87	14.88	-0.14 (e)
F. Precipitated as NH ₄ MgPO ₄ ..	16.50	16.29	16.39	+1.37 (f)

- (a) No silica removed.
- (b) Silica removed.
- (c) Temperature 290—300°.
- (c) (C₁) Temperature 300—330°.
- (d) KOH : HNO₃.
- (e) In ammonium citrate.
- (f) In citric acid.

Conclusion.

The above work emphasises what is already known :—
I.—That the official gravimetric method of determining total phosphoric acid gives high results when phosphoric acid is determined in superphosphate without evaporation of the solution to dryness on a steam bath to remove silica.
II.—That several methods other than the official gravimetric give equally good results in half the time.

THE WORLD'S POTASH.

OLD AND NEW SOURCES OF SUPPLY.

THE potash hitherto used in this country has been chiefly derived from the enormous deposits of potash salts which occur near Stassfurt, in the North of Germany. These deposits have been systematically and economically worked and the trade so well organised that German potash on account of its cheapness became the almost exclusive source of the potash required throughout the world. The German source being no longer available it has become necessary to take stock of other sources of supply, and these are considered in "The World's Supply of Potash," a pamphlet just issued by the Imperial Institute.

In this pamphlet, which forms in fact a miniature encyclopædia of its subject, both the old and new sources of potash are described so far as details are available. Certain of these will probably only be utilised so long as the price of potash continues high, but others promise to become active competitors with the Stassfurt deposits even when prices again fall to their usual level.

The chief use of potash, usually in the form of the

chloride or sulphate, is as an artificial manure, for which purpose over 90 per cent of the world's output is employed. But potash is also essential for numerous chemical industries carried on in this country and for the manufacture of the finest kinds of glass, and the present scarcity is having considerable effects on these industries. The increased production of potash in the United Kingdom from kelp and other vegetable sources referred to in this pamphlet is now under serious consideration.

The price of "The World's Supply of Potash" is one shilling post free, and application for copies, enclosing remittance, should be made to the Imperial Institute, South Kensington, S.W.

POTASH FROM QUEENSLAND "PRICKLY PEAR."

IN the account given by the *Brisbane Courier* of the recent visit of Parliamentarians and others to the property of the Cactus Estates Company, at Dulacca, Western Queensland, where measures are being conducted for the destruction of the prickly pear pest on a large scale by the use of arsenious trichloride, some particulars are given of the work done in recovery of potash.

Mr. O. C. Roberts, the inventor of this method of prickly pear destruction, and who is now directing operations on a block of 10,000 acres of infested land, gave the following information to the press representatives. He stated that a year ago they picked up the ash from five acres, and got from it half a ton of 80 per cent potassium carbonate per acre. That was worth about £22 a ton in America at the time. At present the railway freight would absorb a lot of the profit, but he believed the Government would meet the settlers in the matter by reducing the rates, as it would assist the country in getting clear of the pear. The Germans had a complete monopoly of the potash business, and since the war potash had jumped from £22 to £90 per ton. He confidently believed that within the next five or six years Queensland would begin to take its place as a big potash exporting country. For the last couple of centuries Sweden and other countries had been leaching ashes which contained 6 per cent of potash, while prickly pear ash yielded 15 per cent of potash. They would be astonished to find the quantity of ash got from the pear. He had taken as much as seven tons per acre, including wood ash. They had designed a machine to pick up the ash on the vacuum principle. It was only intended to take up 50 per cent of the ash, and if rain came before it was gathered it would leach the potash out of it. It was proposed, after the pear and timber had been burnt and the ash gathered, to sow Rhodes grass on the ground. He was told by practical men that Rhodes grass would crowd out any further growth of pear, but if it did not they could put fire through the grass and burn it off. He believed potash would solve the problem of clearing the pear on a lot of land which at present it would not pay to touch, and that the potash would pay for the clearing.

SCHEME FOR THE ORGANISATION AND DEVELOPMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH.*

1. THERE is a strong consensus of opinion among persons engaged both in science and in industry that a special need exists at the present time for new machinery and for additional State assistance in order to promote and organise scientific research with a view especially to its application to trade and industry. It is well known that many of our industries have since the outbreak of war suffered through our inability to produce at home certain

* Presented to both Houses of Parliament by command of His Majesty.

articles and materials required in trade processes the manufacture of which has become localised abroad, and particularly in Germany, because science has there been more thoroughly and effectively applied to the solution of scientific problems bearing on trade and industry and to the elaboration of economical and improved processes of manufacture. It is impossible to contemplate without considerable apprehension the situation which will arise at the end of the war unless our scientific resources have previously been enlarged and organised to meet it. It appears incontrovertible that if we are to advance or even maintain our industrial position we must as a nation aim at such a development of scientific and industrial research as will place us in a position to expand and strengthen our industries and to compete successfully with the most highly organised of our rivals. The difficulties of advancing on these lines during the war are obvious and are not under-estimated, but we cannot hope to improvise an effective system at the moment when hostilities cease, and unless during the present period we are able to make a substantial advance we shall certainly be unable to do what is necessary in the equally difficult period of reconstruction which will follow the war.

2. The present scheme is designed to establish a permanent organisation for the promotion of industrial and scientific research.

It is in no way intended that it should replace or interfere with the arrangements which have been or may be made by the War Office or Admiralty or Ministry of Munitions to obtain scientific advice and investigation in connection with the provision of munitions of war. It is of course obvious that at the present moment it is essential that the War Office, the Admiralty, and the Ministry of Munitions should continue to make their own direct arrangements with scientific men and institutions with the least possible delay.

3. It is clearly desirable that the scheme should operate over the kingdom as a whole with as little regard as possible to the Tweed and the Irish Channel. The research done should be for the kingdom as a whole, and there should be complete liberty to utilise the most effective institutions and investigators available, irrespective of their location in England, Wales, Scotland, or Ireland. There must therefore be a single fund for the assistance of research under a single responsible body.

4. The scheme accordingly provides for the establishment of:—

(a) A Committee of the Privy Council responsible for the expenditure of any new moneys provided by Parliament for scientific and industrial research;

(b) A small Advisory Council, responsible to the Committee of Council and composed mainly of eminent scientific men and men actually engaged in industries dependent upon scientific research.

5. The Committee of Council will consist of the Lord President, the Chancellor of the Exchequer, the Secretary for Scotland, the President of the Board of Trade, the President of the Board of Education (who will be Vice-President of the Committee), the Chief Secretary for Ireland, together with such other Ministers and individual members of the Council as it may be thought desirable to add.

The first non-official members of the Committee will be:—

The Right Hon. Viscount Haldane of Cloan, O.M., K.T., F.R.S.,

The Right Hon. Arthur H. D. Acland, and

The Right Hon. Joseph A. Pease, M.P.

The President of the Board of Education will answer in the House of Commons for the sub-head on the Vote, which will be accounted for by the Treasury under Class IV., Vote 7, "Scientific Investigations, &c."

It is obvious that the organisation and development of research is a matter which greatly affects the public educational systems of the kingdom. A great part of all research will necessarily be done in universities and

colleges which are already aided by the State, and the supply and training of a sufficient number of young persons competent to undertake research can only be secured through the public system of education.

6. The primary functions of the Advisory Council will be to advise the Committee of Council on—

- (i) proposals for instituting specific researches;
- (ii) proposals for establishing or developing special institutions or departments of existing institutions for the scientific study of problems affecting particular industries and trades;
- (iii) the establishment and award of Research Studentships and Fellowships.

The Advisory Council will also be available, if requested, to advise the several Education Departments as to the steps which should be taken for increasing the supply of workers competent to undertake scientific research.

Arrangements will be made by which the Council will keep in close touch with all Government Departments concerned with or interested in scientific research, and by which the Council will have regard to the research work which is being done or may be done by the National Physical Laboratory.

7. It is essential that the Advisory Council should act in intimate co-operation with the Royal Society and the existing scientific or professional associations, societies, and institutes, as well as with the universities, technical institutions, and other institutions in which research is or can be efficiently conducted.

It is proposed to ask the Royal Society and the principal scientific and professional associations, societies, and institutes to undertake the function of initiating proposals for the consideration of the Advisory Council, and a regular procedure for inviting and collecting proposals will be established. The Advisory Council will also be at liberty to receive proposals from individuals and themselves to initiate proposals.

All possible means will be used to enlist the interest and secure the co-operation of persons directly engaged in trade and industry.

8. It is contemplated that the Advisory Council will work largely through sub-committees, reinforced by suitable experts in the particular branch of science or industry concerned. On these sub-committees it would be desirable as far as possible to enlist the services of persons actually engaged in scientific trades and manufactures dependent on science.

9. As regards the use or profits of discoveries, the general principle on which grants will be made by the Committee of Council is that discoveries made by institutions, associations, bodies, or individuals in the course of researches aided by public money shall be made available under proper conditions for the public advantage.

10. It is important in order to secure effective working that the Advisory Council should be a small body, but it is recognised that even if full use is made by the Council of its power to work through reinforced sub-committees, its membership may be found inadequate to do justice to all the branches of industry in which proposals for research may be made or to the requests of other Government Departments for assistance. It is therefore probable that it will be found necessary to strengthen the Council by appointing additional members.

The first members of the Council will be:—

The Right Hon. Lord Rayleigh, O.M., F.R.S., LL.D.,

Mr. G. T. Beilby, F.R.S., LL.D.,

Mr. W. Duddell, F.R.S.,

Prof. B. Hopkinson, F.R.S.,

Prof. J. A. McClelland, F.R.S.,

Prof. R. Meldola, F.R.S.,

Mr. R. Threlfall, F.R.S.

With Sir William S. McCormick, LL.D., as
Administrative Chairman.

11. The Advisory Council will proceed to frame a

scheme or programme for their own guidance in recommending proposals for research and for the guidance of the Committee of Council in allocating such State funds as may be available. This scheme will naturally be designed to operate over some years in advance, and in framing it the Council must necessarily have due regard to the relative urgency of the problems requiring solution, the supply of trained researchers available for particular pieces of research, and the material facilities in the form of laboratories and equipment which are available or can be provided for specific researches. Such a scheme will naturally be elastic and will require modification from year to year, but it is obviously undesirable that the Council should live "from hand to mouth" or work on the principle of "first come first served," and the recommendations (which for the purpose of estimating they will have to make annually to the Committee of Council) should represent progressive instalments of a considered programme and policy. A large part of their work will be that of examining, selecting, combining, and co-ordinating rather than that of originating. One of their chief functions will be the prevention of overlapping between institutions or individuals engaged in research. They will, on the other hand, be at liberty to initiate proposals and to institute inquiries preliminary to preparing or eliciting proposals for useful research, and in this way they may help to concentrate on problems requiring solution the interest of all persons concerned in the development of all branches of scientific industry.

12. An Annual Report, embodying the Report of the Advisory Council, will be made to His Majesty by the Committee of Council and laid before Parliament.

13. Office accommodation and staff will be provided for the Committee and Council by the Board of Education.

ARTHUR HENDERSON.

July 13, 1915.

AMERICAN CHEMICAL SOCIETY.

SEATTLE MEETING.

THE Fifty first Meeting of the American Chemical Society will be held in Seattle, Washington, on Tuesday, August 31, to Friday, September 3, inclusive. A complimentary dinner by the Science Faculty of the University of Washington to the members of the Council, followed by a business meeting, will be held at the Hotel Frye on August 30, at 7 p.m.

The Opening Meeting will be at Meany Hall, Campus of the University of Washington. Headquarters: Hotel Frye, corner Third Avenue and Yesler Way, European plan. The Arctic Club, located across Prefontaine Square from headquarters, will keep open house to delegates.

A feature of the meeting will be two symposiums by the Industrial Division, one a general symposium completing the symposium at New Orleans and especially devoted to the progress of chemistry in special lines of chemical industry. Papers have been promised pointing out the influence of the chemist upon the following industries, and his accomplishments therein:—

Iron and Steel—George W. Sargent.
Iron and Steel—A. S. Cushman.
Perfumery—Alois von Isakovics.
Perfumery—E. T. Beiser.
Lead—G. W. Thompson.
Paints and Varnishes—Maximilian Toch.
Petroleum—David T. Day.
Illuminating Gas—Sidney Mason.

A symposium will also be held on the Distillation of Wood, papers having been promised by the following experts in this line: J. R. Withrow, J. E. Teeple, Marc Darrin, Charles H. Herty, Bailey Tremper, and Newton Critus.

General Programme of Meeting.

Monday, August 30.

7. 0 p.m.—Council dinner.

Tuesday, August 31.

10. 0 a.m.—Address of welcome by Henry Suzzalo, President of University of Washington. Response by Charles H. Herty, President American Chemical Society. Address, "Chemical Industry," by Dr. Leo H. Baekeland. Response, "Industrial Resources and Opportunities of the Pacific North-West," by Dr. H. K. Benson.

1.30 p.m.—Symposium Industrial Division.

8. 0 p.m.—Complimentary Smoker by Seattle Commercial Club.

Wednesday, September 1.

10. 0 a.m.—Division meetings, Campus.

1.30 p.m.—Division meetings, Campus.

4.30 p.m.—Automobile trip over boulevards.

8. 0 p.m.—President's Address, President Charles H. Herty. Business meeting.

Thursday, September 2.

Excursion on Puget Sound.

8. 0 p.m.—Subscription banquet (place to be arranged), price 3 dols.

Additional Programme for Women.

August 31, 3. 0 p.m.—Reception and tea, University Campus.

" " 8. 0 p.m.—Organ recital (to be arranged).

September 1, 10. 0 a.m.—Automobile ride through parks and boulevards.

NOTICES OF BOOKS.

Programme of the City and Guilds Technical College, Finsbury, 1915.

THIS programme for the Session 1915-16 contains full information about the courses of instruction and fees at the City and Guilds Technical College, and also gives abstracts of the regulations of the Institutions of Civil Engineers, Mechanical Engineers, &c. Details of the courses of work at the Institute are included with syllabuses of the lectures and time tables, and the programme shows that the training given is thoroughly well planned and systematic and that a high standard of work is expected from the students.

Metropolitan Borough of Poplar. Annual Report for the Year 1914. By FREDK. WM. ALEXANDER.

THE annual report of the Medical Officer of Health for Poplar contains, amongst the usual tables and statistics, further details of the manufacture of electrolytic disinfecting fluid, which the Council continues to find most economical and satisfactory. In spite of adverse criticisms the process has been a success for eight years, and plants for the manufacture of magnesium hypochlorite have been installed by other corporations in England and abroad. It is noteworthy that the Portsmouth Corporation is electrolysing sea-water for disinfecting purposes, and their example is likely to be followed by other seaside towns—to the great benefit of inhabitants and visitors.

Progress in Preventive Medicine in Pennsylvania since the Creation of a State Department of Health. Harrisburg, Pa.: Wm. Stanley Ray.

THIS number of the monthly health bulletins issued by the Pennsylvania State Department of Health gives a short account of the establishment of the Board and of legislation relating to public health. The admirable organisation of the department is explained, emphasis being laid upon the many educational schemes for which it is responsible. These include the issue of monthly bulletins,

giving information in simple language which the layman can readily understand, the publication of newspaper articles also addressed to readers having no special medical knowledge, the delivery of lectures on preventive medicine and sanitation, &c. By these means the public gets knowledge which prepares them for a large expenditure of funds, and for willing co-operation in schemes for the general welfare of the State. The great activity and excellent work of the department are well shown by the statistics given in the bulletin relating to the lowering of the death rate.

Soils of Massachusetts and Connecticut with Especial Reference to Apples and Peaches. By HENRY J. WILDER. Washington: Government Printing Office. 1915.

THIS bulletin contains an account of the surface features, the nature of the soil, and the climate of Massachusetts and Connecticut. Contour maps are given, and the descriptions of the soils are fairly full. The general history and prospects of orcharding are discussed, and some account is given of cultural methods as applied to apples and peaches. The relation of soil characters to crop and varietal adaptation is the subject of a brief discussion, and the bulletin will be a useful guide to the farmer or intending settler in the district.

Coal-tar Products and the Possibility of Increasing their Manufacture in the United States. By HORACE C. PORTER. Washington: Government Printing Office. 1915.

OWING to the interruption of trade caused by the European war the imports of coal-tar products into the United States have been very greatly reduced, and the Bureau of Mines has seized the occasion to point out in this bulletin how some comparatively neglected industries may be developed. Statistics of the production and disposal of coal-tar, benzol, &c., are given, and a brief outline of the classification and derivation of aniline dyes and the preparation of phenol and various miscellaneous chemicals and drugs. The bulletin also includes a short account of the use of coal-tar products in making explosives and an interesting article on the commercial and economic phases of the coal-tar situation. In this article the establishment of chemical industries for the manufacture of refined coal-tar products is shortly discussed, and a brief report is given of the meeting of American manufacturers in September, 1914, to consider the situation; at this meeting two admirable suggestions were made—that if a foreign patent is not used within a reasonable period it should be open to use by American manufacturers and that dumping should be prohibited by legislation.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clx. No. 26, June 28, 1915.

New Series of Compounds of Tetravalent Platinum (Pentaminochloroplatinic).—L. Tschugaeff and N. Wladimiroff.—It is well known that the number of molecules of ammonia corresponding to one atom of tetravalent platinum in the series PtCl_6K_2 , $\text{PtCl}_5\text{NH}_3\text{K}$, &c., can vary from 0 to 6. According to Werner and Miolati, as the amount of ammonia increases the molecular conductivity μ diminishes to a minimum and then increases. The minimum value is 0 for the salt $\text{PtCl}_4 \cdot 2\text{NH}_3$. Hitherto the compound containing five molecules of ammonia has not been prepared, but the authors have now succeeded in

filling this gap, and have shown that $\text{Pt}[\text{5NH}_3\text{Cl}]\text{Cl}_3$ can be obtained by the action of liquid ammonia upon ammonium chloroplatinate in absence of water. The reaction readily takes place in sealed tubes at the ordinary temperature, the product being a mixture of two substances which can be separated by crystallisation. The less soluble is the chloride of the Drechsel-Gerdes base, $\text{Pt}_6\text{NH}_3 \cdot \text{Cl}_4$, while the other is the chloride of the new base. In this new base only three atoms of chlorine are ionised, while the fourth is intimately bound to the atom of platinum. A series of salts corresponding to the general formula $\text{Pt}_5\text{NH}_3\text{Cl}_x$ exists; for example, the nitrate can be obtained by precipitating the solution of the chloride with concentrated nitric acid. It is less soluble than the chloride, and the atom of chlorine it contains gives no precipitate with nitric acid even on boiling. The trivalence of the ion has been confirmed by the determination of the molecular conductivity of the salts and by their capacity for coagulating at known concentration colloidal solutions of arsenic trisulphide. The salts of the pentaminochloroplatinic series yield those of Reiset's base $[\text{Pt}_4\text{NH}_3]_2\text{X}_2$ by reduction with zinc and very dilute hydrochloric acid.

MISCELLANEOUS.

Determination of Small Quantities of Hydrocyanic Acid.—Arno Viehoveer and Carl O. Johns.—In their work on cyanogenetic plants the authors found it necessary to estimate small quantities of hydrocyanic acid. The various titration methods and the silver gravimetric method could not be used, as the plant distillates usually contain reducing compounds. The colorimetric thiocyanate method is not sufficiently accurate. After studying the conditions influencing the formation of Prussian blue the authors recommend the following method of carrying out the estimation:—The solution to be tested is first made slightly alkaline by the addition of 0.02 to 0.1 gm. of sodium hydroxide. It is then concentrated in a round-bottom 200 cc. flask, by using a vacuum pump and condenser. The flask is immersed in a water-bath kept below 70°, and the concentration is continued till less than 1 cc. of liquid remains. 0.2 to 0.5 cc. of 3 per cent freshly prepared ferrous sulphate solution and about 0.05 of potassium fluoride are then added. The flask is exhausted by means of a water vacuum pump, the contents are mixed by rotating the flask, and after five or ten minutes 30 per cent nitric acid is added. The blue colour appears at once, or, if only traces of HCN are present, it may be necessary to warm to 50° on the water-bath. The suspension is then diluted to a volume which would give a colour intensity convenient to compare with a suspension of Prussian blue made from a known weight of potassium cyanide. Any considerable excess of ferric salts should be avoided in testing for a cyanide. The method furnishes a very delicate qualitative test for a cyanide, 0.00002 gm. of KCN being detected by it.—*American Journal of Pharmacy*, 1915, lxxxvii., No. 6.

NOTES AND QUERIES.

Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Barium Sulphide.—A correspondent wishes to be furnished with the address of manufacturers or dealers in barium sulphide (powder). He is desirous of buying this in 28 lb. lots, and knowing that formerly this chemical came chiefly from the Continent, he is at loss as to where this can be obtained in Great Britain.

Lithium Chloride.—A few weeks ago a letter was published in the CHEMICAL NEWS referring to the large quantity of lithium chloride running to waste in the hot spring at the Wheal-Clifford Mine in Cornwall. Can we get into touch with the owner of this property? We think it might be practicable to devise a means of recovering this lithia in one form or another.—M. B.

THE CHEMICAL NEWS.

VOL. CXII., No. 2907.

A DISCREPANCY IN GEOCHEMICAL DATA.

By H. S. SHELTON.

ABOUT four years ago (CHEMICAL NEWS, 1910, cii., 75) I called attention to a striking discrepancy between the quantity of sulphate stated to be present in river waters and the possible sources from which it could be obtained. I gave some reasons for thinking the error to be in the sulphate analyses. Recently (CHEMICAL NEWS, 1914, cx., 307) in reply to criticism I stated some other reasons for the same opinion, and promised further data at an early date. The present paper is a continuation of the arguments relating to the discrepancy, and contains some of the promised data.

The statistics in this paper are derived almost entirely from Clarke's "Data of Geochemistry" (Bull. No. 491, U.S. Geological Survey). This has been done for two reasons. One is that the statistics of the U.S. Survey have been compiled with considerable labour, are drawn from a wide area of experiment, and are as a whole undoubtedly the best extant. The other is that the principal criticism of my first paper has come from a member of the Survey, and it will thus save dispute if I base my contention so far as possible on statistics that originate from the Survey Office. I desire to say, however, that while the fact that I use any particular statistics implies that I have every reason to think that they are accurate enough for the purpose, I reserve the right to criticise or amend them on a future occasion should further investigation show sufficient ground for so doing.

In my previous paper I dealt almost entirely with the possible sources of river water sulphate. I now propose to lay considerable stress on the manner of disposal of any sulphate that may reach the sea. I will therefore first call attention to Table I., showing a relation between the marine salts and the substances carried by the rivers to the sea:—

TABLE I.
(Adapted from Clarke's "Data," p. 125).

	A.	B.	C.
	Metric tons $\times 10^3$	Metric tons $\times 10^{12}$	
CO ₃	961,350	95.6	I
SO ₄	332,050	3,553	II
Cl	155,350	25,538	164
Br	—	86.8	—
NO ₃	24,614	—	—
Na	158,357	14,130	89
K	57,982	510.8	9
Ca	557,670	552.8	I
Mg	93,264	1,721	18
Al ₂ O ₃ , Fe ₂ O ₃	75,213	—	—
SiO ₂	319,170	—	—

A. The estimated annual addition of each radicle by the rivers to the sea.

B. The estimated amount of saline matter in the ocean.

C. Quotient in millions of years, showing the time that would be taken for the amount to accumulate at the present rate.

In quoting this table I wish to make clear that I am not deducing from it conclusions which imply that the figures are strictly accurate. The estimates of the amount of matter dissolved in sea water appear to me to be within reasonable limits reliable, but I am of opinion that the data contained in the first column should be accepted with considerable reserve. The present paper, however, is not concerned with the question of the general accuracy of

geochemical data, the point under discussion being the presence of a discrepancy, glaring and patent, which is out of all proportion to the ordinary probable general sources of inaccuracy. The inferences that I am drawing on this point merely presuppose a rough-and-ready approximation and are not invalidated by small statistical errors.

Treated in this way the table concerning all the factors but one shows a correspondence between the size of the quotient and the known facts of chemical erosion and deposition. It will particularly be noted that with one exception all the substances of which considerable quantities are carried to the sea are either important constituents of the sedimentary rocks or are present in the sea in such large quantities as to imply that the amount has been accumulating for very many millions of years.

Of the constituents mentioned the sodium and the chlorine are present in the sea in such quantities that we need not now consider them. Calcium carbonate is deposited over a considerable fraction of the ocean floor. The greater part of the silica, alumina, and iron is probably precipitated on contact with the salt water and reappears in the shales. Moreover, great quantities of silica are accounted for by silicious organisms, the fossils of which are found in flints and similar deposits. The magnesium finds its way into the dolomites. It seems to be established that large quantities of potassium are absorbed in the region intermediate between the terrigenous and oceanic deposits and reappears in the sedimentaries as glauconite and other common minerals. I do not attempt in any of these instances to establish a quantitative equivalence between the salts carried by the rivers to the sea and the deposition in the sedimentaries. I am merely pointing out that as a matter of known fact all the substances I have named do normally find their way back to the sedimentaries properly so called. With the possible exception of potassium they are all known to do so in such enormous quantities as to render further inquiry superfluous.

To this general rule sulphur in the form of sulphate is a prominent and outstanding exception. According to theory the sulphate radicle or its equivalent of sulphur should be deposited on the ocean floor six times as rapidly as the potassium, more than three times as rapidly as the magnesium, about one-third as rapidly as the carbonate; actually there is no evidence that any appreciable quantity of sulphur or of sulphate is deposited in the ordinary sedimentaries. Evidence of continuous deposition is entirely lacking.

To emphasise this statement it will be well to mention briefly the only two suggestions to the contrary which have to my knowledge been made. The first, published by Prof. Joly, I have already dealt with in my previous paper (CHEMICAL NEWS, 1910, cii., 75) and no further comment is required. The second has been made to me privately on very high authority. It is that by the agency of living organisms the sulphate is reduced to sulphide, which is either deposited as such or evolved as sulphuretted hydrogen. Some reaction of the kind is said to have been noted in the Black Sea. But once again the same objection applies. The widespread sedimentary deposit containing any considerable proportion of sulphur has yet to be discovered. Also the greater part of the sulphuretted hydrogen if it were formed would be returned directly by the rain to the sea. The formation of either sulphide or sulphuretted hydrogen from marine sulphate as apart from organic matter has yet to be proved.

Another statement made by some geologists calls for mention here. It is stated in some text-books that the particles of sandstone rock are sometimes welded together by calcium sulphate, and it would follow that such sulphate would in some way or other come from the sea. Such a statement is rendered highly improbable by the analyses of sandstone rock. None of the ordinary unaltered sandstones analysed by the U.S. Geological Survey (Bull. No. 419 and others) contain any appreciable

quantity of sulphate, and so far as I am aware there is no evidence whatever for the contention that the majority of sandstones contain calcium sulphate. The metamorphoses and changes incidental to sedimentary rock are so various that in exceptional cases no constituent however rare can be asserted to be invariably absent from any rock whatever; consequently it would be absurd to say dogmatically that sulphate is never found in sandstone, but it can positively be stated that any that may be present does not normally come from deposition by the sea; any possible exceptional case, therefore, is not relevant to the problem we are discussing.

There is in fact only one known means by which any large quantity of marine sulphate returns to the sedimentaries. In cases where considerable areas drain into enclosed lakes the small quantity of sulphate normally found in river waters is reinforced by marine salts carried by the wind from the sea into the drainage area. Such a process is occurring now in the Dead Sea and elsewhere. When an arm of the sea by some geologic change becomes a closed basin the same result follows. Such are the recognised sources of salt beds, and in these deposits calcium sulphate is, next to sodium chloride, probably the most considerable constituent. A reference to the table will show, however, that as the sulphate in the sea is present in a smaller proportion than the chloride, so the sulphate deposits will be expected to be less in amount than the chloride. There is no reason to assume that the proportion actually found differs greatly from that indicated by theory.

To sum up this side of the argument, it is clear that not only is the quantity of sulphate stated to be carried to the sea so great that its ultimate disposal is an unsolved problem, but if the actual amount were even a third or a quarter of the estimated amount the problem would still exist.

The above statement leads naturally to the consideration of the possible sources of the sulphate stated to be present in river water. As this was the subject of my original paper and has been the occasion of some controversy (CHEMICAL NEWS, 1910, cii., 175; 1914, cx., 307; 1915, cxi., 126) a brief summary of the previous argument with such additions as are suggested by recent work should suffice. The basal assumption on which the whole paper rests is simply and solely that erosion is a continuous process. The process of weathering implies that rock is attacked chemically by the action of air or water, a portion is carried away in solution, the remainder is washed away in suspension; both parts ultimately find their way down the rivers to the sea. There are, needless to say, many exceptions and qualifications to this simple statement of the process of erosion. In the case of limestone it is highly probable that the greater part is carried in solution. Again, a portion of the solvent action of water is carried out underground, and it is obvious that the removal of the suspended matter cannot immediately follow. But the assumption on which geochemical calculations must be made is I think that such processes average themselves out. The exceptional solubility of limestone rock is balanced by the exceptional insolubility of sandstone, sandstone chemically being igneous rock from which a considerable portion of the calcium has been removed. The underground solvent action of water is balanced by the presence in surface strata of portions of rock and soil already eroded partially or entirely, and thus carried more readily to the sea in suspension. All these qualifications do not affect the fact that, *if a sufficiently wide area be taken*, there is a limit that can be assigned to the amount of any element that can be carried to the sea in solution. If we average the composition of the rocks, the limit is the amount of the element eroded each year. Assuming a reasonable degree of accuracy in the data of the U.S. Geological Survey and of other geological bodies, all that is required to find this limit is the percentage of any element in the earth's crust subject to erosion, and the ratio between total erosion and solvent erosion. The product

of the two is the outside limit of the percentage of any element which can be present in river waters. The limit will never actually be obtained because some portion of all elements, though the solubility will vary, is carried to the sea in suspension. In my previous paper I took the ratio as 5 : 1, a number based on the researches of Mellard Reade, the proportion of sulphur in the crust of the earth subject to erosion as 0.2; expressed as SO_4 this becomes 0.6. The percentage of sulphate in the soluble content of river water should not therefore be greater than $0.6 \times 5 = 3$. The percentage stated to be present was 8.22. (In the second edition of the "Data of Geochemistry" the percentage is given as 12.14!) Therefore five-eighths of the alleged sulphate was unaccounted for.

Now let us examine these data in the light of recent knowledge. The weakest point in the previous calculation was the ratio between solvent and general denudation. With regard to solvent denudation, for lack of fuller data I took Mellard Reade's result for England and Wales, and extrapolated on the assumption that England and Wales was a sufficiently large area. Nevertheless this ratio is confirmed by other researches and statistics. A number of other considerations show that the ratio errs, if at all, on the side most favourable to the contention of the paper. Let us take the case of a single area, the Mississippi Basin. The rate of sedimentary erosion is calculated by Humphreys and Abbott as 1/6000 feet per year, or 1/1500 of the weight of the water in which it is suspended (Geikie, "Geology," p. 494). The salinity of the Mississippi is 166 parts per million (Clarke's "Data," p. 70), or 1/6000 of the weight of the water. The ratio of solvent erosion to total erosion is therefore 1 : 5, exactly as previously put forward. Clarke's estimate for the solvent erosion of the whole world is 1/32,833 feet per year. Sollas' estimate for the sedimentary erosion of the whole world is 1/2400 feet per year. Comment is needless. I am of opinion that Sollas' estimate is too high, but, to obtain the ratio here provisionally accepted, it would have to be reduced to $\frac{1}{30000}$ feet per year! It is possible that Mr. Dole would maintain a lower ratio than 1 : 5, but it is difficult to see how one much smaller can be maintained. A ratio of 1 : 4 or even 1 : 3, while it would create difficulties with regard to the calcium, would not remove the discrepancy with regard to the sulphate.

The conclusion of the argument, therefore, is that (with the exception of the radicle CO_3 , which comes partly from atmospheric CO_2 and of chlorine, which is mainly sewage and cyclic salt) the percentage of no constituent in river water, assuming that all the particular element is carried in solution, can exceed five times its percentage in the rocks. Actually, in the case of sulphur the percentage must be less, as some sulphur is carried to the sea in suspension. Clarke's analysis of Mississippi silt shows 0.07 per cent sulphur and some sulphate. Assuming that the sulphate is in reality derived from sea water, it will be seen that the percentage of sulphur does not differ greatly from that stated to be present in the rocks. One other statement, to avoid undue length in the present paper, I must make without giving full reasons. It helps my case, but is not necessary to it. A study of the U.S. Survey analysis of rocks convinces me that even the minute percentage allowed for sulphur in the average composition of the rocks is too large. Glaring as is the discrepancy, the figures understate it.

To show how the 5 to 1 ratio works out in practice, it will be interesting to repeat Table II., showing the average composition of the rocks, and to put underneath Clarke's latest estimate of the matter dissolved in river waters.

Table III. is contained in the second edition of Clarke's "Data of Geochemistry," but has been copied verbatim from Mr. Dole's paper (CHEMICAL NEWS, 1911, ciii., 289).

A simple formula for finding roughly the average composition of rock subject to erosion is to multiply the figures for limestone by 4, sandstone by 12, igneous rock

by 20, and shale by 64; add together and mark off two decimal places. Any reader sufficiently interested can do the calculation for himself. It is obvious that in every case except those mentioned the relation holds. The percentage of each of the constituents in the rocks exceeds one-fifth of the percentage in the soluble content of river water. The extreme case of the carbonate radicle, which is known to be partly obtained from atmospheric carbon dioxide, gives the result—rock analysis 4.04 per cent $\text{CO}_2 = 5.4$ per cent CO_3 , which multiplied by 5 gives 27 per cent instead of 35.5, a not very large difference. (There is also a slight deficiency in the calcium, which would disappear, as would the carbonate deficiency if the proportion of limestone were taken as higher. But this assumption is not necessary). Sulphur gives the result—rock analysis 0.17 per cent sulphur = 0.51 per cent SO_4 , which multiplied by 5 gives 2.55 instead of 12.14. *Nearly four-fifths of the sulphate radicle is unaccounted for.* The discrepancy is great and glaring, considerably more so than was stated in my previous article.

TABLE II.

	Igneous rocks.	Shale.	Sandstone.	Limestone.
SiO_2	59.87	58.1	78.33	5.19
Al_2O_3	15.0	15.4	4.77	0.81
$\text{Fe}_2\text{O}_3, \text{FeO}$	5.98	6.47	1.37	—
MgO	4.06	2.44	1.16	7.89
CaO	4.79	3.11	5.55	42.57
Na_2O	3.39	1.31	0.45	0.05
K_2O	2.93	3.24	1.31	0.33
Water	1.96	5.0	1.63	0.77
CO_2	0.52	2.63	5.03	41.54
S	0.11	0.26 (a)	0.07	0.11
Other constituents	1.47	1.66	0.33	0.74
	100	100	100	100

(a) Expressed as 0.64 SO.

Table II. is taken from the first edition of Clarke's "Data," but subsequent calculations do not differ in any relevant particulars.

TABLE III.

Average Composition of the Inorganic Matter in Rivers of the World.

Silica, SiO_2	11.67
Oxides of iron and aluminium, $\text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3$	2.75
Calcium, Ca	20.39
Magnesium, Mg	3.41
Sodium, Na	6.40
Potassium, K	1.51
Carbonate radicle, CO_3	35.15
Sulphate radicle, SO_4	12.14
Nitrate radicle, NO_3	0.90
Chlorine, Cl	5.68
Minor constituents	—
	100

I do not think it necessary here to repeat the consideration of the infinitesimal additions that need to be made on account of other possible sources of SO_4 radicle. It is obvious that on the most favourable assumption, allowing to them the greatest possible significance, the discrepancy is so great that they are hardly worth mentioning in comparison.

One other point remains for discussion. Mr. Dole (CHEMICAL NEWS, 1915, cxi., 87) asked me to investigate the discrepancy "by comparing the chemical composition of the river waters not only with the chemical composition of the crust of the earth, but also with the composition of that part of the crust which is now subject to the disintegrating action of water, and, further, that he consider not only the absolute quantities of the chemical constituents in the crust, but their relative solubility as well." The latter part of the sentence if applied to the sulphur is

so glaring an error and shows so amazing an incapacity in what is supposed to be his own subject that it can be left to expose itself. The data on which my argument is based and the course of the argument are no doubt open to criticism, but I think it will be generally accepted that, however soluble any substance may be, the river water cannot carry to the sea more than is there. (It is a somewhat strange paradox that the factor of solubility might be admitted in the case of calcium carbonate in a manner in which it would be ridiculous in the case of sulphur. Anyone interested in these questions will have no difficulty in solving the paradox). The argument is based on the assumption, the incorrect assumption, that all the sulphur is carried in solution, none in suspension. In so far as the assumption is incorrect—in my opinion to some considerable extent—the discrepancy to which I am calling attention is all the more glaring.

The second part of Mr. Dole's sentence is very badly expressed. Taking it in conjunction with his previous paper (CHEMICAL NEWS, 1911, ciii., 288) I take it to mean that human agency has so altered the strata subject to erosion and so increased the proportion of sulphate in the eroded areas that any consideration of general erosion ceases to apply. It would imply that while normally the percentage of sulphate in river water is, say, 1 per cent, it is now, owing to human agency, 12 per cent. It is unfortunate that Mr. Dole is unable or unwilling to state his contention in intelligible form, but the sentence means either this or nothing bearing on the discussion. I do not propose to overburden the present paper with a full discussion of this point, nor do I propose to attempt to assess the exact effect due to human agency. I am, of course, perfectly aware that if by opening a mine you allow water from the surface to drain through beds of coal or bituminous shales, and then pump the stagnant water into the local streams, you may find a small stream highly charged with sulphate; also, if the mine is in a range of hills, the interior water of which can drain into the adjacent valley, a similar though smaller effect will occur; also, if land is manured with substances containing some proportion of sulphur, some sulphate may find its way into the rivers. (A good soil, well manured, is calculated to contain roughly 0.023 grm. sulphur per kilogram). While I should be the last to underestimate the importance of human agency in modifying the geologic conditions of erosion and sedimentation, there is no evidence whatever that this particular discrepancy can be so explained. The amount of sulphate due to human agency is no doubt great if measured in tons, but no one I think will attach to this factor very great importance in view of Prof. Clarke's estimate of 332 million metric tons of sulphate or 110 million metric tons sulphur as the annual contribution of the rivers to the sea. In such a matter as this the burden of proof lies with the other side. I shall, therefore, only put forward the following instances of sulphate analyses in districts not the centres of large populations. It will be seen that the proportions of the sulphate radicle are still of the same inexplicable order.

TABLE IV.

(The numbers in the second column are references to the pages in Clarke's data).

River.	Analyst.	Date.	Sulphate, per cent.	Salinity, total solid.
Dwina..	Roth (95)	—	18.95	187
Amazon.	P. F. Frankland (83)	—	7.37	59
Plata ..	Kyle (83)	1875	7.69	91
Yuhon..	Steiger (78)	1905	10.75	98

The conclusion of the whole argument is, therefore, that the proportion and amount of sulphate radicle in river waters is grossly overestimated. If the amount of sulphate radicle annually carried to the sea were 100 millions of tons instead of three times the amount, it would still be difficult to account for its source and its disposal. As it is the glaring nature of the discrepancy is clear and in-

disputable. In view of the many experimental difficulties which arise in analysing correctly the amounts of the substances dissolved in water containing about 1/10,000 of its weight of dissolved matter, I think it probable that there is some constant error or errors in sulphate determinations. I would particularly call attention to the two probable causes I have already pointed out. The first is the gross error that arises when water is evaporated by means of the gas-burner. The second and more important is that a barium salt insoluble in hydrochloric acid does not necessarily imply sulphate. It seems not unlikely that some unknown compounds, probably complex silicates, have the same property. In any case the conclusion is very plain and very important: *Whenever river or spring water is analysed by present methods it is highly probable that the analysis is grossly unreliable.* There are one or two alternative explanations of the facts stated in this paper which are theoretically possible, but the one I have put forward is the most probable.

The next step in the investigation is experimental work. I am not myself engaged in analytical investigation, and have not as yet had time and opportunity to investigate the matter experimentally. In case I am not able to do so, I propose to state the fact in the columns of the CHEMICAL NEWS, and to leave the matter open to any able and willing to take it up.

P.S.—To obtain the full arguments in favour of the view here stated, it is advisable to read not only this paper but the others, of which this is a continuation. The original paper contains one or two misprints. Weighed estimates for *weighted* estimates and magnetic for *magnetic* are the most important.

THE ANALYSIS OF PLATINUM.*

By F. MYLIUS and A. MAZZUCHELLI.

AMONGST the platinum metals which are of such great importance in physical research, platinum itself occupies a prominent position, as, being the possessor of sharply defined properties, it is much used for fundamental measurements.

Although the way of preparing pure platinum has been known for a long time, the technical method never gives absolutely pure metal. The chemical control of its degree of purity is very important for scientific reasons, but is very difficult to carry out with the means at present known.

This need for surer methods of analysis is not limited to the nominally pure metal, but also extends to the different modifications of commercial platinum, which is used for various utensils in technics. As the economical durability of them is greatly influenced by the presence of small quantities of various constituents in the metal, the question of their analytical estimation is one of considerable practical importance. In Lunge's standard "Chemisch-technischen Untersuchungsmethoden" (1905) the subject is hardly mentioned. However, in the short section on platinum on p. 169 is to be found the statement, "At the present time it is known that the accurate separation of the individual platinum metals from one another is attended with great difficulties." In Classen's "Ausgewählten Methoden der Analytischen Chemie" (1901) the methods of separation are collected with great care. The analysis of platinum alloys, platinum ore, and platinum residues is comprehensively treated, but no practicable method of investigating commercial platinum is to be found.

A short introduction to the analysis of commercial platinum which is given in Muspratt's "Handbuch der Technischen Chemie" (1900, vol. vii.) is limited to the approximate determination of iridium, and thus affords no sufficient characterisation of the metallic material.

Among the many methods of the analytical investigation of the platinum alloys that of St. Claire Deville and Debray is pre-eminent for its reliability; it is known to have been used for the analysis of the specimens for the determination of the international masses and weights, and it allows of unsurpassable accuracy; but it is very complicated, and it is not suited for the rapid orientation of commercial platinum.

When the impurities to be detected in the platinum are small in amount fused lead cannot be used as a separating agent, especially as the impurities in the lead would be added to the material under examination. Mylius and Foerster have for some time been engaged in the investigation of small impurities in platinum; but their carbon monoxide process, which leaves the impurities in the residues while the platinum is volatilised as carbonyl chloride, is hindered by the presence of iridium, and thus cannot be taken into account for analysing commercial platinum.

In spite of this apparent lack of a suitable "analytical process" there is no want of methods for the separation of the individual platinum metals. The obvious thing to do was to arrive at a satisfactory method of "proximate analysis" for technical platinum by a suitable combination of reliable methods of precipitation. The expression "proximate analysis" is here used instead of the now unsuitable words "technical analysis," in contradistinction to "accurate analysis," and refers to determinations of a moderate, but from a practical point of view sufficient, accuracy.

Nominally pure and technical platinum do not show sharply defined differences from one another, but are connected by transition products. Analytically they are to be regarded from the same point of view.

The critical examination of impure platinum is closely connected with the question of the preparatory purification of platinum, for there is no prospect of determining minute quantities of constituents unless the metal itself can be separated from solutions in the form of a pure substance.

I. PREPARATORY PURIFICATION OF PLATINUM.

Amongst the salts which can be employed for the separation of platinum the much used ammonium platinum chloride has given only moderately successful results, because this difficultly soluble double salt always carries down with it in its precipitation small quantities of impurities (especially iridium). The same may be said of the corresponding potassium platinum chloride. The readily soluble sodium platinum chloride, $\text{Na}_2\text{PtCl}_6 + 6\text{H}_2\text{O}$, has been found to be unequally efficient; it shows only a slight tendency to form mixed crystals.

If Finkener's directions are followed and the complex salt is crystallised from weak soda solution, when the iridium tetrachloride is converted into trichloride, according to Mylius and Foerster (*Ber.*, 1892, xxv.a, 665) the preparation can be thoroughly purified, and a platinum metal free from impurities can be obtained.

This method of purification has been successfully used in technics for twenty years when perfectly pure platinum has been required.

It may be noted here that the sodium double chloride when isolated always contains excess of sodium chloride, especially as it is washed with a solution of this salt. We have found that it can easily be freed from it if it is finally re-crystallised from alcohol, and thus the purification is completed. In this method use is made of the property of the double salt observed by Precht (*Zeit. Anal. Chem.*, 1879, 509), namely, that its solubility in absolute alcohol is greater than in 95 per cent alcohol, and the salt is precipitated from the solution by means of water.

The sodium platinum chloride containing salt is first completely dehydrated at 120°. The powder thus obtained is then washed into a flask with double its weight of absolute alcohol, in which the double salt readily dissolves at room temperature, while the sodium chloride remains

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PLATINUM METALS AS CHLORIDES.
(Reactions of grm.-litre Solutions).

Reagent	Palladium, PdCl ₂ .	Rhodium, RhCl ₃ .	Platinum, PtCl ₄ .	Iridium, IrCl ₄ .	Ruthenium, RuCl ₄ .	Osmium, OsCl ₄ .
1. Colour	Brownish yellow.	Red.	Pale yellow.	Dark brown.	Dark brown.	Golden yellow.
2. H ₂ S at 18° in one minute	Immediate brown precipitate.	No precipitate.	No precipitate.	Decoloration without precipitate.	No precipitate.	No precipitate.
3. Saturation with H ₂ S at 80° in one minute	Blackish brown separation.	Blackish brown separation.	Blackish brown precipitate.	Slight brownish turbidity.	Blue-black separation.	Black separation.
4. Ethyl mercaptan solution, 1:100, on warming	Immediate yellow precipitate.	Yellow slowly.	Light yellow precipitate, slowly.	Slow decoloration without precipitate.	Brown slowly.	No decoloration nor precipitate.
5. KI solution, 1:1000	Immediate dark brown precipitate.	Unchanged.	Red-brown precipitate, slowly.	Immediate yellow coloration.	Unchanged.	Unchanged.
6. NH ₃ solution, on warming	Immediate decoloration.	Slow decoloration.	Slow decoloration.	Immediate light coloration.	Greenish dark coloration.	Yellowish brown precipitate.
7. Saturation with ammonium chloride	No precipitate.	No precipitate.	Yellow precipitate.	Black precipitate.	Brown precipitate.	Red precipitate.
8. Potassium sulphocyanide solution, 1:100, on warming	Unchanged.	Yellow coloration.	More intense yellow coloration.	Decoloration.	Dark violet.	Unchanged.
9. Na ₂ CO ₃ (neutralisation and warming)	Turbidity due to yellowish brown oxide.	Yellow coloration.	Unchanged.	Yellow coloration.	Turbidity due to black-brown oxide.	Black precipitate.
10. Then sodium hypochlorite solution	Brown precipitate of peroxide.	Blue-green coloration by dioxide.	Unchanged.	Blue precipitate of dioxide.	Yellow solution; smell of ozone.	Light solution; smell of per-osmium acid.
11. Mercury cyanide	White flocculent precipitate.	Unchanged.	Unchanged.	Unchanged.	Unchanged.	Unchanged.
12. Hydrazine hydrochloride solution, 1:1000	Blackening owing to separation of metal.	Yellow coloration.	Blackening owing to separation of metal.	Yellow coloration.	Yellow coloration.	Unchanged.
13. Dimethylglyoxime solution, 1:1000	Immediate yellow precipitate.	Unchanged.	Unchanged.	Unchanged.	Unchanged.	Unchanged.
14. Luteo-cobaltchloride in HCl solution	Unchanged.	Reddish precipitate.	Unchanged.	Brownish precipitate.	Unchanged.	Unchanged.

behind. It is then filtered into a second flask in which water is placed to the amount of about 15 per cent of the alcohol in the filtrate. The liquid as it flows in solidifies at once to a thick crystalline paste from which the yellow needles of the hydrated pure compound $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ can easily be isolated by means of a suction apparatus. The alcohol still remaining in them rapidly volatilises in the air.

(NOTE.—While cold alcohol has no action on pure sodium platinum chloride it energetically decomposes the salt if foreign platinum metals are present, aldehyde and acetic acid being formed. Black insoluble substances are formed, especially on warming. A rule must therefore always be made of acidifying with hydrochloric acid alcoholic platinum chloride solutions before evaporation.)

The small quantities of double salt contained in the mother-liquor can easily be obtained by evaporation (after acidification with hydrochloric acid).

The reduction to metal is usually performed by heating the double salt in a current of hydrogen, and extracting the sodium chloride. It can also be effected in the wet way by electrolysis, or by hydrazine hydrochloride, if the latter is free from impurities. The reaction also takes place (this is at variance with the statements in literature, "Gmelin-Kraut," 1914, [7], v., 42) even in the presence of a great excess of free hydrogen chloride.

Special attention may here be called to the fact that the difficultly soluble precipitates of platinum ammonium chloride, made by igniting on platinum, are well suited for this reduction in the wet way.

The yellow powder is suspended in ten times its weight of water made slightly acid with hydrochloric acid, and the mixture is warmed in a dish with gradual addition of a solution of hydrazine hydrochloride. If the liquid is stirred from time to time the reaction begins with the complete solution of the double salt to a clear brownish liquid (with transitory separation of a flocculent precipitate of lower oxide). In a later phase of the reaction gas is evolved, and the reduced platinum separates from the liquid in a more or less compact state on the side of the dish, while the supernatant liquid gets gradually paler. By regulating the addition of the hydrazine solution and the rise of temperature the velocity of the reaction can be arbitrarily altered.

In circumstances which will be described later the reduced platinum may contain appreciable quantities of chloride or lower chloride, which are decomposed on ignition. Small amounts of iridium which might be present in the platinum ammonium chloride remain more completely dissolved with any platinum in the liquid, the more acid the liquid was in this reduction process.

II. THE ANALYTICAL DETECTION OF THE PLATINUM METALS.

1. Qualitative Reactions of the Grm.-litre Solutions.

From what has been said above it will be seen that there is no prospect of determining the very small amounts of other constituents in platinum unless the large excess of the metal itself is first removed. The next task is then to reduce these constituents to a small volume, and to separate them from one another after suitable concentration. In the case of the platinum metals, even more than with the other elements, the quantitative separation depends upon an accurate knowledge of the qualitative reactions of their solutions. The scientific treatment of the platinum metals in literature only occasionally gives an opportunity of obtaining a comparative view of the differences in question. For this reason it seemed to us appropriate to observe the most important reactions of the platinum metals in solutions containing equal quantities by weight, and to give the following summary of them.

Comparable grm.-litre solutions were chosen, which contain a grm. of the metal as chloride in a litre. Their low concentration is favourable for the accurate observation of the differences in the reactions. Such solutions

have also been found very useful for comparative observations in the analysis of other heavy metals.

The liquids used contain the metals in the state of chlorination (or oxidation) which mostly occurs in analysis. Palladium is dissolved as dichloride, rhodium as trichloride, platinum, iridium, ruthenium, and osmium as tetrachlorides with hydrochloric acid.

The grm.-litre solutions were prepared as follows:—

(1). *Platinum*.—One grm. of the pure metal was converted in the usual way into H_2PtCl_6 . The residue, free from nitric acid, obtained by evaporation was dissolved in water to make 1 litre.

(2). *Palladium*.—The quantity of crystallised palladous chloride ($2 \cdot 002$ grms. $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$) corresponding to 1 grm. of metal was dissolved in water to make 1 litre.

(3). *Rhodium*.—The quantity of ammonium rhodium chloride ($3 \cdot 8561$ grms. $(\text{NH}_4)_3\text{RhCl}_6 \cdot 1 \cdot 5\text{H}_2\text{O}$) corresponding to 1 grm. of metal was repeatedly evaporated with dilute aqua regia, and finally with hydrochloric acid; the residue, free from ammonium chloride, was made up to 1 litre with water, after the addition of 50 cc. of concentrated hydrochloric acid.

(NOTE.—The ammonium rhodium chloride was prepared by saturating a solution of sodium rhodium chloride with ammonium chloride and slowly crystallising.)

(4). *Iridium*.—The quantity of ammonium iridium chloride ($2 \cdot 2882$ grms. $(\text{NH}_4)_2\text{IrCl}_6$) corresponding to 1 grm. of metal was repeatedly evaporated with dilute aqua regia, and finally with hydrochloric acid: after the addition of 50 cc. of concentrated hydrochloric acid to the residue, which was free from ammonium chloride, it was made up to 1 litre with water.

(5). *Ruthenium*.—The quantity of per-ruthenic acid ($1 \cdot 6293$ grms. RuO_4) corresponding to 1 grm. of metal was dissolved in 50 cc. of concentrated hydrochloric acid and the solution made up to 1 litre with water.

(NOTE.—In the evaporation of RuO_4 described by Gutbier and Rauschoff (*Zeit. Anorg. Chem.*, 1905, xlv., 260), the weighing of any desired quantity can be performed in stoppered glass vessels, they can be opened under concentrated hydrochloric acid, and diluted to a suitable volume according to the weight.)

(6). *Osmium*.—The quantity of ammonium osmium chloride ($2 \cdot 3031$ grms. $(\text{NH}_4)_2\text{OsCl}_6$) corresponding to 1 grm. of metal was treated with 100 cc. of concentrated hydrochloric acid and made up to 1 litre with water.

2. Colorimetric.

According to this summary each platinum metal gives some reactions which are different from those of the other metals, and which can be used in their presence for qualitative detection.

The coloration of the chloride solutions is characteristic. The solutions of platinum and osmium are yellow, of palladium brownish yellow, of rhodium red, of iridium and ruthenium dark brown. The colorations of the grm.-litre solutions are, however, not quite constant, but alter somewhat with the age of the solutions owing to increasing hydrolysis. A colorimetric comparison with the solutions of the chlorides of other heavy metals is interesting. It is, however, of value only if the hydrogen chloride concentrations in the different solutions as well as the concentrations of the metallic chloride in question are nearly the same and are also high, as otherwise hydrolysis causes great discrepancies. Decigram.-litre solutions are then prepared from the grm.-litre solutions by diluting with ten times the amount of 37 per cent (fuming) hydrochloric acid; these solutions contain the metallic chlorides in concentrated hydrochloric acid. Such solutions can be kept for colorimetric purposes. If solutions of the following are placed in similar test-tubes—Copper (as CuCl_2), iron (as FeCl_3), nickel (as NiCl_2), cobalt (as CoCl_2), and gold (as AuCl_3), and if they are arranged (independently of the shade of colour), according to the obvious intensity of the coloration the following series is obtained:—Platinum, pale yellow; nickel, pale yellow; gold, pale

yellow; palladium, pale yellow; rhodium, rose-red; cobalt, sky-blue; copper, golden yellow; iron, golden yellow; osmium, golden yellow; ruthenium, brown; iridium, brown. There can be no doubt about the position of the last members, but there may be a difference of opinion about the places of rhodium and cobalt, according to the subjective impression.

The depth of colour of platinum chloride is the least, and hardly half that of gold chloride.

The almost equal colour intensity of the copper, iron, and osmium solutions is more than ten times as great as that of the platinum and nickel solutions; this may be seen by comparing them with centigram.-litre solutions of iron, copper, and osmium, specially prepared by diluting with concentrated hydrochloric acid. It will be seen that they are rather more strongly coloured, though the shade is essentially the same.

According to this superficial discussion the colorimetric determination of the individual platinum metals as chlorides is not hopeless, if concentrated hydrochloric acid is used as solvent, which Hüttner (*Zeit. Anorg. Chem.*, 1914, lxxxvi., 341) found convenient in his experiments on cobalt, iron, and copper.

The rose-red coloration of rhodium chloride solution is specially characteristic, but it is very much influenced by hydrolysis. The gram.-litre solution containing more water used in the summary is more yellowish red, owing to the admixture of a yellow modification of the chloride.

With iridium and ruthenium chlorides the effect of hydrolysis upon the colour of the solutions is also appreciable.

In time aqueous solutions of iridium chloride deposit blue dioxide. Osmium chloride is also similarly decomposed hydrolytically, giving a dark hydroxide.

Owing to the great colouring power of the brown iridium tetrachloride it is easy to estimate the actual amount of iridium in a technical platinum colorimetrically from the coloration of its hydrochloric acid chloride solution (just as the cobalt in a technical cobalt can be determined colorimetrically by Hüttner's method). It can easily be done with a centigram. of metal, which is dissolved in aqua regia, and then the residue after evaporation is freed from nitric acid and diluted to 100 cc. with concentrated hydrochloric acid. The decigram.-litre solutions of pure platinum and pure iridium, also prepared with concentrated hydrochloric acid, are then put together until the colour of the mixture is the same as that of the solution under examination. The proportions by volume of the solutions gives approximately the proportion by weight of iridium to platinum in the technical metal. The coloration is only slightly affected by very small quantities of other impurities.

The colorimetric determination of rhodium by means of the rose-red chloride solution is, on the other hand, very dependent upon the impurities; it can be employed only when the rhodium solutions are comparatively pure.

(To be continued).

THE VAPOUR PRESSURE OF CONCENTRATED SUGAR SOLUTIONS.*

By D. ORSON WOOD, B.Sc., A.R.C.Sc.

THE measurement of the vapour pressure of highly concentrated solutions is of considerable importance from the point of view of the theory of solution; for it is only when the strength of the solutions used becomes great that the exact form of the theory can be determined. The depression of vapour pressure is usually deduced from experiments on osmotic pressure or freezing-point, and very few measurements of the vapour pressure itself have been made. This is largely due to the difficulty of taking observations of sufficient exactness to enable the difference

between the vapour pressures of the solution and the solvent to be obtained without relatively large errors.

In 1912 Dr. Perman and Mr. T. W. Price read a paper before this Society, in which they gave the results of a large number of experiments made by an air-current method. Their data showed variations in the relative lowering of vapour pressure which were unexpected from theoretical considerations, and, in consequence, Prof. A. W. Porter suggested to me that it would be useful to attempt measurements by a different method in order to confirm or modify their conclusions. Preliminary results obtained with a very concentrated sugar solution of unknown strength did not agree with Dr. Perman's values, and the following paper contains an account of further observations made on solutions of saccharose. The measurements are by no means as accurate as one could wish, but they are probably the best which have been obtained so far with highly concentrated solutions.

Method.

After a critical examination of the air-current method it seemed difficult to point to any definite source of error other than that possibly introduced by the use of the perfect gas equation in the calculation of the vapour pressure from the experimental data (for example, see a letter in *Nature*, March 11, 1915, from Lord Berkeley). This being the case, it seemed desirable to use a direct method which should give the pressures without the necessity of any such calculations. Moreover, the point of immediate interest was the variation of the Babo constant (*i.e.*, the lowering of the vapour pressure relative to that of the solvent) with temperature, and the direct static method lends itself very easily to the determination of the vapour pressure at different temperatures.

The more serious objections usually put forward against the method are (see, for example, Lincoln and Klein, *Journ. Phys. Chem.*, 1907, p. 11):—

(a) That with so small a quantity of vapour any impurity would produce a large error.

(b) That, since evaporation takes place from the upper layers only, they become too concentrated and the measured vapour pressure is too small.

With regard to (a) the most serious impurity is dissolved air. The removal of this air under the condition that the concentration of the solution must be known constitutes the main difficulty of the experiment. The method used for removing the air would, however, also remove any traces of other volatile substances, should they ever be present. As for (b), even at the highest temperatures only a small quantity of vapour is evolved, and by stirring the solution electromagnetically the objection is sufficiently overcome. Apart from these possible sources of error there is the disadvantage that the preparation of the apparatus for each solution is somewhat laborious, so that the method does not lend itself easily to making experiments with many different solutions.

It is necessary, then, to introduce an air-free solution of known concentration into a vessel in which its vapour pressure can be measured barometrically. After many trials the arrangements shown in Figs. 1 and 2 were adopted. The solution was prepared in the vessel depicted in Fig. 1, and from this vessel it was transferred to the main apparatus (Fig. 2), where its vapour pressure was measured. The part of this latter to the left of the constriction A is required only during the filling process, and when that is completed it is sealed off.

The Preparation of the Solution.—The filler consists of a glass bulb blown at the end of a piece of wide glass tubing, about 10 inches long, which serves as a condenser. The tubes c and d are fused to the end of this condenser—c having at its upper end the inner portion of the ground-glass joint through which the filler is ultimately joined to the main apparatus at c' (Fig. 2). In the preparation of a solution the condenser tube was first cut in two at E, and the two parts thoroughly cleaned with chromic acid. The acid was rinsed out with water, then ammonia, and finally

* A Paper read before the Faraday Society, May 11, 1915.

this was removed with distilled water. The two parts were next dried in a hot-air oven, and were then ready for the solution. A quantity of clear saccharose crystals were picked by hand from the main stock, and a known mass of them placed in the bulb which was then fused to the upper part of the filler again. The air was removed with a pump, and the vessel and its contents weighed on a chemical balance. In the meanwhile ordinary distilled water was thoroughly boiled in a tube similar to that shown in Fig. 1, except that the branch D was absent. After it had cooled this vessel was inverted and connected to the filler with a short piece of pressure-tubing attached to the end of c. The taps being opened, the requisite amount of "air-free" water was allowed to enter the filler. In this way a solution, at least 3 per cent more dilute than that ultimately required, is obtained, and it contains a minimum of air to be removed in subsequent operations.

The bulb was next connected, at D, through suitable drying tubes, to the air-pump, and was carefully warmed. The taps c and D were shielded as far as possible from the direct heat with wet blotting-paper. The whole apparatus being exhausted of air, evaporation was continued until the desired concentration was almost reached. Finally, to remove all traces of air the solution was heated to about 100°C . with the tap D closed. After cooling a little, D was opened, and the air which had been evolved was pumped out. This process was repeated several times. The bulb was then allowed to cool, and was weighed. The mass of the bulb, together with a known mass of crystals, having been determined previously, the mass of the water, and therefore the strength of the solution, was known.

The operations just described needed the utmost care in the manipulation both of the flame and the air-pump, in order that the tendency of the solution to boil by bumping might be kept within reasonable limits.

The Filling Process.—Referring to Fig. 2, the apparatus consists of a bulb F, into which the solution is to be placed, and the arrangement to the right of F, by which the pressure is measured. The wide glass tube H contains the mercury whose meniscus is in contact with the vapour; close to it is a similar tube K, which is just long enough to project over the top of the water-bath in which F, H, and K are immersed. This tube is connected, through an air trap, by flexible rubber tubing to the barometer M. The level of the mercury through the whole system is controlled by a mercury reservoir attached to N. The vapour pressure is sufficient to make the mercury column continuous, and the difference in the level of the mercury at H and M gives the required vapour pressure (subject to a small temperature correction to be discussed later). During the measurements the solution in F is stirred by means of a sealed glass tube containing short rods of soft iron embedded in glass-wool. These iron rods are dragged up and down by a circular electro-magnet just outside the bulb.

In the process of cleaning and filling, F, H, K, and the other rigid parts of the apparatus were firmly fixed to a wooden frame to which the filler tube, sealed on to the rest by the ground joint cc', was also attached. The apparatus was completely exhausted of air through the tube L, and the mercury was allowed to flow into HK from N, thus preventing access of vapour to the more remote portions of the apparatus. The tap in c was then opened, and the solution, driven by gravity and its own vapour pressure, flowed down slowly into F. When sufficient solution had entered the bulb it was sealed off at the constriction A. This was always one of the critical stages in the experiment; but success was rendered quite certain by softening the constriction with a luminous flame before the apparatus was exhausted. This removed any stress that might have been imposed by the attachment of the comparatively heavy filler bulb, and by the subsequent clamping down on to the supporting frame.

In the earlier experiments, as a final precaution, a tube was sealed on at B in a plane perpendicular to that of the rest of the apparatus. This tube was connected to the

pump, and the solution was warmed and stirred in F to remove any residual traces of air, the water vapour evolved being condensed in a bulb surrounded by a freezing mixture.

This water was afterwards distilled back into F; but a little was inevitably drawn into the drying tubes, and the uncertainty thereby introduced into the concentration was considered to overbalance any advantage gained by the possible removal of last traces of air, of whose presence, moreover, there was never any certain evidence.

The Measurements.

When the tube F had been filled and sealed up successfully, the apparatus was removed from its supporting frame, and was held by an iron clamp so that the tubes A, H, and K were immersed in a water-bath. This con-

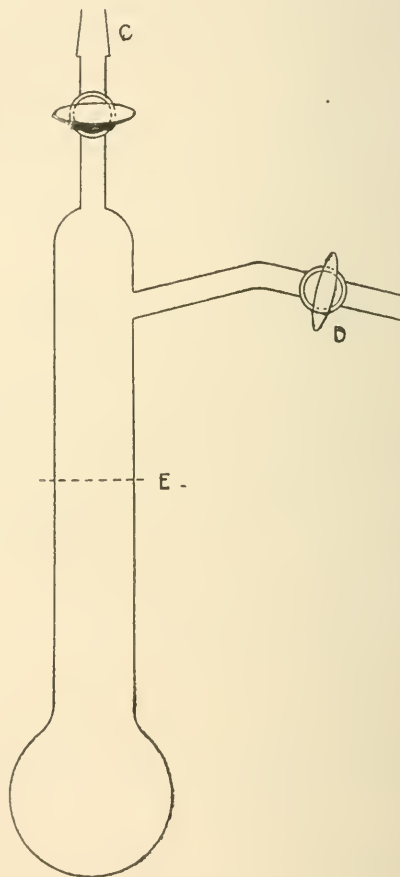


FIG. 1.

sisted of a large copper tank with a plate-glass window, through which the level of the mercury in the tube H could be observed. The bath was heated by two independent gas-burners, one arranged so that its flame could be adjusted very finely in order to keep the temperature constant. The stirring was carried out most efficiently by a single propellor fixed in a corner of the tank and driven at a high speed by an electric motor.

A metre scale was set up in a vertical plane midway between H and M, and the divisions on this scale corresponding to the two mercury levels were read off with two cathetometers used as reading telescopes. The reservoir attached to N was manipulated each time so as to bring the mercury meniscus to about the same level in H.

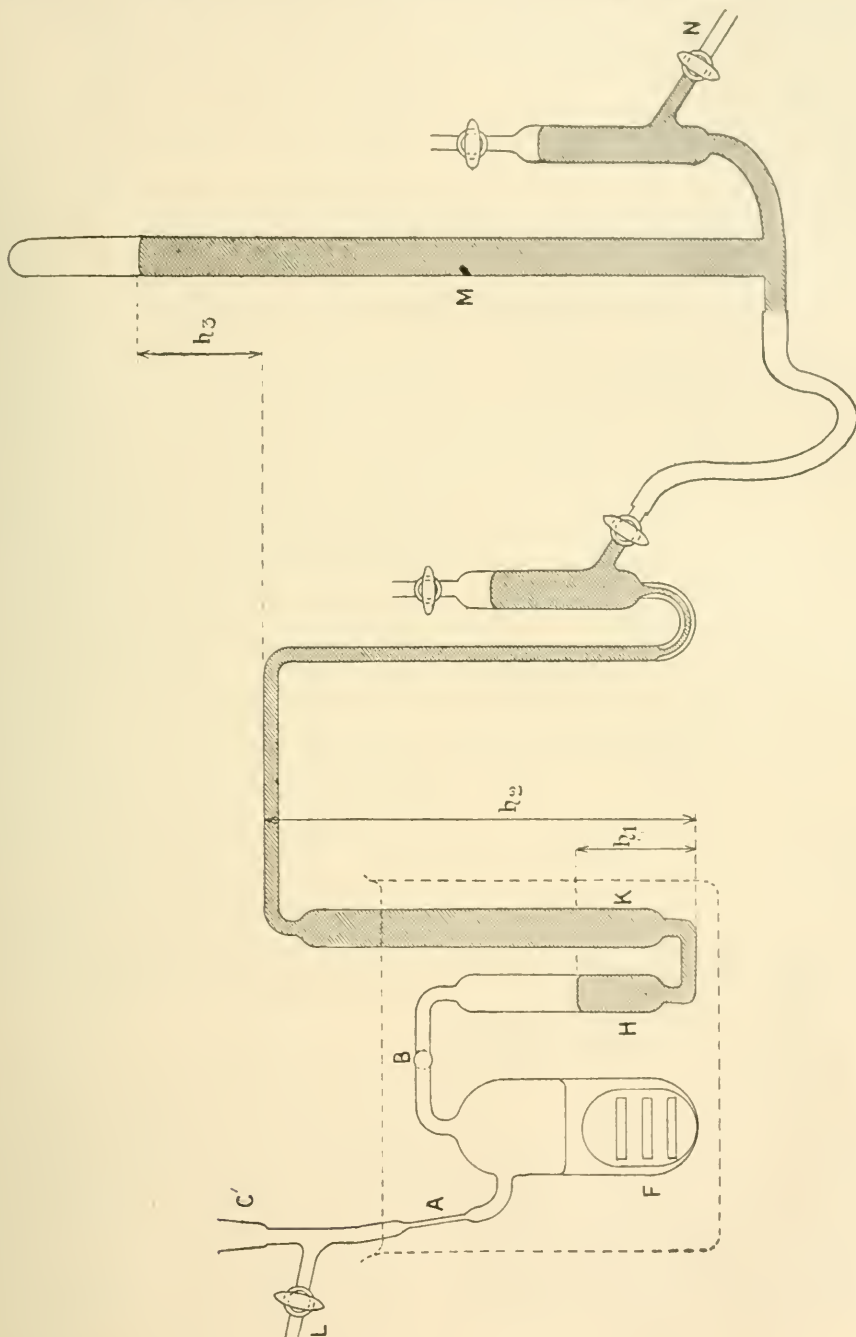


FIG. 2.

The temperatures were determined with a limited-range thermometer (50°C. to 105°C.), divided into tenths and read with a small magnifying lens. The thermometer was afterwards standardised by direct comparison with another limited-range thermometer whose errors were well known. Three other thermometers were necessary—(i.) to determine the average temperature of the emergent stem, (ii.) to measure the temperature in the region between *K* and *M* (the thermometer was suspended between the limbs of the U-tube of the air trap), (iii.) to measure the temperature

of the barometer tube *M*. A screen was set up to protect the mercury columns outside the bath from direct exposure to heat.

The readings were, at first, corrected for the curvature of the meniscus in *H* and in *M*, but as the correction is at the very extreme limit of the possible accuracy and is made very uncertain by the high temperature of the mercury in the tube *H*, it was afterwards omitted altogether. A small correction is, however, necessary to allow for the difference of temperature of the mercury columns connecting *F* and

M. This correction in no case exceeded 0.02 cm. of mercury, as may be seen from the following considerations:—

The true vapour pressure of the solution is given by the expression $h_3\rho_2 + h_2\rho_1' - h_1\rho_1$, while that actually measured is $(h_3 + h_2 - h_1)\rho_2$, where—

ρ_1 = density of mercury at temperature of bath,
 ρ_2 = density of temperature of barometer tubes,
 ρ_1' = mean density of column h_2 ,

and the heights h_1 , h_2 , and h_3 are marked in Fig. 2. The actual measurement is therefore too great by an amount $h_2(\rho_2 - \rho_1') - h_1(\rho_2 - \rho_1)$, which can be written

$\frac{\rho_2 - \rho_1}{\rho_2}(h_2 - h_1)$ in cm. of mercury at 0° C. with sufficient

accuracy for these experiments. The exact value of this correction in one experiment is shown in Table I. It could have been eliminated altogether by arranging a second apparatus similar to the first alongside of it, but containing water instead of the solution.

Readings (several at each temperature) were taken with both rising and falling temperatures and on different days—on one occasion spread over as much as three weeks. No consistent differences developed, as would be expected if the sugar began to invert. The results recorded in this paper range from 60° C. to 90° C.; but readings were obtained at lower temperatures right down to -10° C. The vapour pressure is then insufficient to support the whole length of the mercury column in the tube K, and the pressure was read off from the difference in level of the surfaces in H and K. The values so determined lay excellently on the vapour pressure curve, but the depression at such low temperatures (*i.e.*, below 60° C.) is so small that the proportionate errors made the observations worthless from the theoretical point of view. The readings at 0° C. and below did, however, show that no appreciable amount of air was present in F at these temperatures, though, of course, it might be evolved reversibly as the temperature rose.

(To be continued).

THE VOLUMETRIC FEHLING METHOD USING A NEW INDICATOR.

By A. M. BRECKLER.

THE volumetric Fehling method has been looked on, very unjustly, as inaccurate and unreliable. An inspection of the work of A. W. Peters (*Journ. Am. Chem. Soc.*, xxiv., 928) shows that under the most carefully controlled conditions of the gravimetric method the ability to duplicate reducing sugar determinations is limited to an accuracy of about one part in 200. His dextrose copper ratios fluctuate about a mean value of 0.522 in the range of 25 to 100 mgrms. of dextrose. The highest value is 525 and the lowest is 520, the value in each case being a mean of 4 to 6 determinations. The work of Munson and Walker (*Ibid.*, xxxviii., 663) at times shows departures from the average which are fully as great. In seeking a method of reducing sugar estimation, therefore, an accuracy of one part in 200 is as great as can be expected.

The method here described is dependent on a constant volume at the close of the titration, a constant time of boiling, and the use of sodium monosulphide solution as indicator.

Description of Method.

The Fehling solution used is made up as follows:—

A. Fehling's Copper Solution (Leach, "Food Inspection and Analysis," p. 591): 34.639 grms. of carefully selected crystals of pure copper sulphate dissolved in water and diluted to exactly 500 cc.

B. Fehling's Alkaline Tartrate Solution: 173 grms. of Rochelle salts and 50 grms. of sodium hydroxide are dissolved in water and diluted to exactly 500 cc. The solution of sodium monosulphide is made up by dissolving

4 grms. of crystalline sodium monosulphide in 100 cc. of water. It should be made fresh every day. The test is conducted in a test-tube $8\frac{3}{4} \times \frac{1}{2}$ inch. A wooden clamp for holding this tube should be provided. A spot tile, with six or more cavities, a 10 cc. pipette, some straight pipettes, and a burette for the sugar solution completes the outfit.

To make a determination, 10 cc. of the mixed Fehling solution are pipetted into the test-tube. The sugar solution, which should contain between 200 and 400 mgrms. of dextrose, or an amount of other sugar equivalent in reducing value to these amounts, is then run in, starting with 8.5 cc. The solution is then boiled one minute, counting from the time a bubble of steam first traverses the entire length of liquid. After the addition of 8.5 cc. and boiling the colour is noted. If the solution is very blue the sugar solution may be added 2 cc. at a time, boiling fifteen seconds after each addition. When the solution in the tube is only a faint blue a drop of it is added to two drops of sulphide solution on the tile. The tile is given a slight rotary shake and the colour of the spot noted. It will be seen that the suspended cuprous oxide turns black and settles at once, while the supernatant liquid turns a more or less intense yellow. The sugar solution is now added to the test-tube in smaller portions, depending on the intensity of the yellow coloration, boiling fifteen seconds after each addition. It is usual in this laboratory (Distillers' Laboratory, 503, Kentucky Title Building, Louisville, Ky.) to use 0.4 cc. at this point. As the colour becomes fainter less is added each time, until finally successive additions are only 0.1 cc. each. As soon as no colour is perceived immediately upon the settling of the cuprous compound, the result is read from the burette and the mean of this reading and the previous one taken as the number of cubic centimetres required to reduce the 10 cc. taken. The experiment is then repeated, adding enough water to make the final volume up to 30 cc. and 97 to 98 per cent of the sugar solution required in the previous trial. This is then boiled one and a-half minutes and the exact amount adjusted, which can usually be done in two additions. This final determination should require from four to six minutes from the time the solutions are mixed until the estimation is finished. It will rarely be found that these two determinations differ more than 1 per cent in value from each other. The second determination is the one to be used.

When the approximate amount of sugar is known, as it is in most cases, the first approximation can be made much closer and the two titrations given equal weight.

Notes on the Method.

The time of boiling after half a minute seems to play a comparatively unimportant part. In a series of experiments 99 per cent of the sugar (dextrose) required to reduce a solution was added and the mixture boiled different lengths of time. The amount required for complete reduction was the same whether the first portion was boiled half a minute or one and a-half minutes. Too protracted boiling, however, is undesirable on account of evaporation and exposure to air. Hence the total time of boiling should be kept within one and three-quarters to two and a-quarter minutes.

The desirability of a constant volume in the gravimetric method during the reduction is well known; preliminary experiments showed this plainly. Under the conditions of this method 10 cc. of Fehling solution with a final volume of 50 cc. required as a mean of several determinations 49.3 mgrms. of dextrose for reduction, 10 cc. with a final volume of 30 cc. required 47.6 mgrms. for reduction. By making a preliminary titration, bringing the volume up to a constant amount and adding most of the sugar at once, its reducing values become constant. Even if the reducing values of the 2 or 3 per cent subsequently added vary 20 per cent the results are still within the limits of the method. As can be seen from the difference shown above a variation of 2 or 3 cc. in the final volume may be con-

sidered negligible. The final volume was arbitrarily selected, as it was the greatest volume at which 0.1 cc. of 0.2 per cent dextrose solution would make a distinct change in colour.

A test-tube of the size given prevents much exposure to the air, and its liability to boil over when heated too rapidly prevents excessive evaporation.

Numerous trials were at first made with ferrous sulphocyanide (Ling, Rendle, and Jones, "Allen's Commercial Organic Analysis," fourth edition) and iodide starch mixture (F. F. Harrison, Sutton's "Volumetric Analysis," tenth edition), but it was found that both have a common defect, namely, they become coloured on exposure to air without addition of Fehling solution. Attempts to obviate this destroy their sensibility to a large extent. The writer had used sodium monosulphide for some time for colorimetric copper estimations and was impressed by its sensitiveness. Furthermore, there ought to be no tendency for the reoxidation of the copper on mixing with the indicator, as the medium is a reducing one. After a few minutes a yellow colour will appear, owing probably to solution of some of the copper sulphide. The absence of colour, however, is permanent for sufficient time for an observation to be made, while when copper is unreduced the appearance of the colour is immediate. After the operator has become familiar with the end point, it can be judged very closely by the appearance immediately on addition of the drop. As long as unreduced copper is present a yellowish colour is perceptible without agitation, while when all the copper is reduced the only shade is the reddish brown of the cuprous oxide.

Proteins and metals which give coloured sulphides interfere with the end-point. For the former, the writer boils a measured volume and adds alumina cream while still hot, then cools and makes up to a convenient volume, adding sufficient water to correct for the volume occupied by the alumina. The solution can then be allowed to settle and the clear supernatant liquid used, or if time is an object it may be filtered. This method works very well on most urines and coloured solutions. For removing the metals methods will doubtless suggest themselves.

Results Obtained.

Various dilutions of a sugar solution were made up and given to a member of the staff (without information as to their sugar content), who obtained the following figures:—

No. of cc. used in titration.	Mgrms. total dextrose present.
23.30	47.60
15.65	47.75
11.70	47.60
9.35	47.75

It must be understood that this was not pure dextrose, as the purpose was only to see whether results were constant and independent of the concentration of the titrating solution over comparatively wide limits. The above results were each obtained with one titration besides the preliminary one.

Impure maltose solutions were titrated in a similar manner:—

No. of cc. used in titration.	Mgrms. total maltose present.
23.2	92.8
15.5	93.0
11.6	92.4
9.25	92.5

The following results show the remarkable constancy of results over long periods. The titrations are on 5 cc. of mixed Fehling solution, which was the original manner of using the method, but it was changed to increase the accuracy of the end-point:—

- 6/11/1914—
5 cc. Fehling reduced by 44.43 mgrms. crude maltose.
8/26/1914—
5 cc. Fehling reduced by 44.47 mgrms. crude maltose.

For each value four concentrations were titrated. This constancy is not confined to maltose, but is also true of dextrose. The dextrose factor for 5 cc. in May was 23.6 mgrms. and in August 23.8 mgrms.

The writer advises the standardisation of the Fehling solution by each user, and hence his factor should not be accepted as final. A mean of four determinations on pure glucose from two different sources, in which the maximum variation from the average was ± 0.15 mgrm., gave 47.5 mgrms. dextrose as the value of 10 cc. of a Fehling solution whose copper content had been accurately adjusted by a sodium thiosulphate solution standardised with pure copper. As can be seen, the factors once obtained need be determined only at rare intervals. Pure dextrose, prepared by the Bureau of Standards, is now available for this purpose.

Summary.

The writer describes a modification of Fehling's volumetric method, designed to do away with some of its sources of error.

The use of a new indicator is described, which, so far as is known, is here first used for this purpose.—*Journal of Industrial and Engineering Chemistry*, vii., No 1.

NOTICES OF BOOKS.

Industrial and Manufacturing Chemistry. Volume I.: Organic. By GEOFFREY MARTIN, Ph.D. (Rostock), D.Sc. (Bristol), B.Sc. (London), F.C.S., assisted by many Specialists. Second Edition. London: Crosby Lockwood and Son. 1915.

THE value of this practical compendium of industrial chemistry has been fully recognised by manufacturing chemists, engineers, and works managers, and this second edition has been called for very shortly after the first. Some new sections have been added to it; for example, on the hydrogenation of fats, the manufacture of milk-sugar, the analysis of rubber, and the new synthetic tanning materials. An index has also been added, giving the trade names of the new synthetic drugs, photographic developers, &c. The book is particularly useful owing to the information it gives relating to minor industries, and for the emphasis the authors constantly lay upon subjects and details which require further research in order to elucidate some disputed points or unsolved problems. It is thoroughly practical, and contains very full references to the literature of all countries.

MISCELLANEOUS.

Research in Aniline Black.—The Gold Medal of the Company of Dyers has been awarded to Prof. Arthur G. Green, F.R.S., Professor of Tinctorial Chemistry in the University of Leeds, and to Mr. W. Johnson, M.Sc., a research student of the University of Leeds, for research work in connection with the art of dyeing. The special research, which was the occasion of the award, was an investigation into the constitution of aniline black. The Gold Medal is awarded annually on the recommendation of the Society of Dyers and Colourists.

Physico-chemical Studies of the Synthesis of Chlorophyll.—Albert and Alexander Mary.—When drops of nitrous nitric acid are added to a very strong alcoholic solution of aniline a white deposit, turning pink, is observed. Then much heat is evolved and the mass becomes green. The reaction appears to be $6C_6H_7N + 15O = C_36H_{30}NO_4 + 6H_2O + 5NO$. Towards the end of the reaction nitrous vapours of NO_2 are evolved. This formula presupposes the polymerisation of aniline. When the reaction is over the walls are coloured green or

reddish brown, and an abundant dark residue is left. When shaken with benzene it yields a greenish fluorescent solution tending to turn red in air and in the light, and giving a brownish resinous deposit. When the benzene is evaporated in absence of air, dichroic crystals of synthetic chlorophyll are obtained. Among the essential characteristics of chlorophyll is its dissociation by hydrochloric acid into phyllocyanic acid and phylloxanthine. Both these products may be obtained from synthetic chlorophyll, which also resembles the natural substance in being insoluble in water, soluble in alcohol, ether, petrol, and benzene. The evaporation of benzene solutions of the two substances gives exactly similar crystals. Willstätter's theory that chlorophyll is a complex organo magnesium compound appears to the authors to be untenable. They believe that aniline and chlorophyll are members of the same family, the former containing one molecule of phenyl and the second six. Chlorophyll is thus a polymer of aniline in which the proportions of nitrogen are reduced by a process of oxidation which gives rise to definite quantities of water and nitrogen dioxide. This polymerised oxide shows the characteristic reactions of chlorophyll.—*Moniteur Scientifique*, 1915, v., 121.

Competitions in connection with the Utilisation and Denaturing of Spirit or Alcohol for Industrial Purposes.—With reference to the notice on pp. 8-9 of the *Board of Trade Journal* of April 1 relative to international competitions organised by the Russian Ministry of Finance in respect (1) of methods of utilising spirit or alcohol or their products, and (2) of new substances for denaturing spirit or alcohol, the Board of Trade have now received, through the Foreign Office, from the Russian Ambassador in London, a number of copies (in English) of the conditions governing these competitions. The following is a summary of the conditions:—As regards the first mentioned competition, prizes of 60,000, 30,000, and 10,000 roubles respectively (rouble at par=2s. 1½d.) will be awarded for the invention of a novel means of adapting alcohol for the preparation of such a product as shall by its nature absolutely differ from the spirit from which it is made, e.g., vinegar, ether, chloroform, &c. Three prizes, of 50,000, 20,000, and 5000 roubles respectively will be awarded for the invention of a novel method of utilising spirit for the preparation of a product (e.g., a pharmaceutical or perfumery preparation), of which spirit or its products (sulphuric ether, &c.) will appear as one of its component parts or dissolvent, providing that spirit cannot be extracted profitably from the product. Three prizes of 30,000, 15,000, and 5000 roubles respectively will be awarded for the invention of a novel method of utilising spirit in productions where spirit or its products would serve as temporary intermediary dissolvents of either of the extracted or precipitated materials, e.g., in the manufacture of smokeless powder, artificial silk, &c. Further prizes, ranging from 75,000 to 5000 roubles, will be awarded for the invention or perfection of apparatus for the utilisation of spirit as motive power, fuel, or illuminant. The competition of new substances for denaturing spirit or alcohol is being organised with the object of extending the use of spirit for technical purposes, and accordingly three prizes of 30,000, 15,000, and 5000 roubles respectively are offered for finding novel denaturing materials for improving the existing methods of denaturing which whilst guaranteeing the free use of denatured spirit would obviate any possibility of using it as a beverage. Applications in respect of both of these competitions should be addressed to "L'Administration Générale des Impôts indirects et du Monopole de l'Alcool," Tutchkoff Naberezhnaia, Petrograd, not later than January 1/14, 1916, and must be accompanied by samples. Such applications should be made in the Russian or French languages, and be enclosed in a special envelope bearing an inscription or device of some sort, the name and address of the applicant being submitted under separate cover bearing the same inscription or mark.

Inventors may reserve the right of benefiting by their inventions and of protecting themselves with letters patent. Copies of the full text of the conditions for participating in the two competitions above referred to may be obtained by United Kingdom firms interested on application to the Commercial Intelligence Branch of the Board of Trade, 73, Basinghall Street, London, E.C.

Royal Society for the Encouragement of Arts, Manufactures, and Commerce.—*Peter Le Neve Foster Prize*.—Mr. Reginald Le Neve Foster has presented the Society with a donation of £140 for the purpose of founding a prize in commemoration of his father, Mr. Peter Le Neve Foster, who was Secretary of the Society from 1853 to 1879. The Council have determined to offer the prize for a paper on "Zinc, its Production and Industrial Applications." The prize will consist of a sum of £10 and the Society's Silver Medal. The paper for which the prize is awarded will be read at one of the Ordinary Meetings of the Society. It is expected that some account will be given of the history of the metal, the sources of its supply, its metallurgy, and the various uses to which it has been or may be applied. Intending competitors should send in their papers not later than December 31, 1915, to the Secretary of the Royal Society of Arts, Adelphi, London, W.C. The paper must be typewritten. It may be sent in under the author's name or under a motto, accompanied by a sealed envelope enclosing the name, as preferred. The judges will be appointed by the Council. The Council reserve the right of withholding the prize or of awarding a smaller prize or smaller prizes, if in the opinion of the judges nothing deserving the full award is sent in.

The Institute of Metals.—Autumn Meeting.—The following is a list of the papers that are expected to be submitted at the Meeting of the Institute of Metals, to be held at the Chemical Society, Burlington House, Piccadilly, W., on Friday, September 17, 1915, commencing at 8 p.m.:—

- "The Corrosion of Gun-Metal." By Dr. C. H. Desch.
- "Metallic Crystal Twinning by Direct Mechanical Strain." By Prof. C. A. Edwards, D.Sc.
- "Notes on the Copper-rich Kalkoids." By Prof. Brinton and Prof. S. L. Moyt.
- "The Constitution of Brasses containing Small Percentages of Tin—a Contribution to the Study of the Ternary System, Copper-Zinc-Tin." By Dr. O. F. Hudson and Mr. R. N. Jones, D.Sc.
- (a) "Structural Changes in Industrial Brasses."
- (b) "Hardness of Copper-Zinc Alloys." By Dr. D. Meneghini.
- "Specifications for Alloys for High-speed Superheat Steam Turbine Blading." By Mr. W. B. Parker.
- "The Physical Properties of Metals as Functions of each other." By Mr. A. H. Stuart, D.Sc.
- "Detection of Internal Blow-holes in Metal Castings by Means of X Rays." By Mr. C. H. Tonamy.
- "A Thermostat for Moderate and High Temperatures." By Messrs. J. L. Haughton, M.Sc., and D. Hanson, M.Sc.

Members intending to take part in the discussion of any of the papers can be supplied with a copy on application to the Secretary a week before the meeting. Copies of all papers will be available at the meeting for the use of members, and those who are unable to attend will subsequently be supplied on application with a copy of any paper of which prints remain. In order that as much time as possible shall be available for discussion the papers will be taken as read. Each speaker will be limited to five minutes in the discussion unless the time should be extended by the meeting. Speakers who are unable to give more than a summary of their views in the time available may send a written statement to the Secretary for publication in the *Journal*. Such statement must be in the hands of the Secretary within a month after the meeting.

THE CHEMICAL NEWS.

VOL. CXII., No. 2908.

NOTES ON GERMAN CHEMICAL NOMENCLATURE.

By E. L. KENNAWAY, M.D., D.Sc.

PROBABLY at the present time German chemical literature is receiving quite as much attention in this country as was the case before the war, owing to the necessity for the production here of substances which have hitherto been prepared chiefly in Germany. It is hoped that the notes given below may be of some service to chemists who have not up till now been familiar with German chemical nomenclature.

Elements.

Bor	Boron
Brom	Bromine
Chlor	Chlorine
Chrom	Chromium
Eisen	Iron
Fluor	Fluorine
Jod	Iodine
Kalium	Potassium
Kohlenstoff	Carbon
Kupfer	Copper
Mangan	Manganese
Natrium	Sodium
Phosphor	Phosphorus
Platin	Platinum
Quecksilber	Mercury
Sauerstoff	Oxygen
Schwefel	Sulphur
*Silicium	Silicon
+Stickstoff	Nitrogen
Wasserstoff	Hydrogen
Wismut	Bismuth
Wolfram (symbol W)	Tungsten
Zinn	Tin

(1). Compounds consisting of two elements are in many cases named by the simple juxtaposition of the names of the two elements.

Schwefelnatrium ..	Na ₂ S
Schwefelwasserstoff ..	H ₂ S
Bromwasserstoff ..	HBr
Arsenphosphor ..	AsP

(2). When a compound consisting of two elements is of the nature of a salt, a nomenclature similar to the English is used in addition to that given under (1) above.

Jodkalium, Kaliumjodid ..	KI
Fluorsilicium, Siliciumfluorid ..	SiF ₄
Schwefelkohlenstoff, Kohlenstoffdisulfid ..	CS ₂
Chlorkohlenstoff, Kohlenstofftetrachlorid ..	CCl ₄

Oxides.

(1). When an element forms two oxides only, these are in some cases distinguished (a) by the names -oxydul and -oxyd, (b) by a nomenclature similar to the English.

Quecksilberoxydul, Mercuriooxyd ..	Hg ₂ O
Quecksilberoxyd, Mercurioxyd ..	HgO
Zinnoxid, Stannooxyd ..	SnO
Zinnoxid, Stannioxyd ..	SnO ₂

(2). When an element forms more than two oxides these are distinguished by various methods.

* In the names of silicon compounds the word Kiesel is frequently used in place of silicium; e.g., Kieselwasserstoff, SiH₄; Kieselsäure, H₂SiO₃.

† Sometimes abbreviated to Stick- in names of compounds.

(a). The names -oxydul and -oxyd can be combined, as are the corresponding terms in English.

Eisenoxydul, Ferrooxyd ..	FeO
Eisenoxydoxydul, Ferriferrooxyd ..	Fe ₃ O ₄
Eisenoxyd, Ferrioxyd ..	Fe ₂ O ₃
Manganooxydul, Manganooxyd ..	MnO
Manganooxydoxydul ..	Mn ₃ O ₄
Manganoxyd, Manganioxyd ..	Mn ₂ O ₃
Manganperoxyd, -superoxyd ..	MnO ₂

(b). The prefixes di-, tri-, &c., are used, but the lowest oxide in many cases bears the name -oxydul only.

Wismutoxydul, BiO
Wismuttri-, di-, pentoxyd.

(3). It will be convenient to state here the nomenclature of acids corresponding to the various oxides, since the latter may be spoken of as anhydrides of the acids.

Stickstoffoxydul ..	N ₂ O	Untersalp Petrigesäure ..	HNO
Stickstoffoxyd ..	NO		
Stickstofftrioxyd ..			
Salp Petrigesäure ..	N ₂ O ₃	Salp Petrigesäure ..	HNO ₂
anhydrid ..			
Stickstofftetroxyd ..	N ₂ O ₄		
Stickstoffpentoxyd ..			
Salpetersäure ..	N ₂ O ₅	Salpetersäure ..	HNO ₃
anhydrid ..			
Kohlenoxyd ..	CO		
Kohlendioxyd ..	CO ₂	Kohlensäure ..	H ₂ CO ₃

Other acids are named in the same way as above, the names of the corresponding oxides presenting no difficulty.

Unterschweflige ..	-	Unterchlorige ..	-
säure ..	H ₂ S ₂ O ₄	säure ..	HClO
Schweflige ..	H ₂ SO ₃	Chlorigesäure ..	HClO ₂
Schwefelsäure ..	H ₂ SO ₄	Chlorsäure ..	HClO ₃
Ueberschwefelsäure ..	H ₂ S ₂ O ₈	Ueberchlorsäure ..	HClO ₄
Tellurigesäure ..	H ₂ TeO ₃		
Tellursäure ..	H ₂ TeO ₄		

Hydroxides.

These are distinguished in the same way as oxides.

Eisenhydroxydul, Ferrohydroxyd ..	Fe(OH) ₂
Eisenhydroxyd, Ferrihydroxyd ..	Fe ₂ (OH) ₆

Salts.

(1). When an element forms two sulphides or halogen compounds, these are distinguished in the following way.

Eisensulfür, Ferrosulfid ..	FeS
Eisensulfid, Ferrisulfid ..	Fe ₂ S ₃
Antimonsulfür ..	Sb ₂ S ₃
Antimonsulfid ..	Sb ₂ S ₅
Antimonchlorür ..	SbCl ₃
Antimonchlorid ..	SbCl ₅

Similarly ... fluorür, ... bromür, ... jodür.

(2). Other salts are named by two methods; either (a) in the same manner as in English, or (b) by a method introducing the name of the corresponding acid; chlorides are not usually named by this latter method.

Kaliumnitrat, salpetersaures Kalium ..	KNO ₃
Kaliumpermanganat, übermangansaures Kalium ..	KMnO ₄

Similarly chlorsaures,* überchlorsaures, borsaures Kalium, &c.

Salts of organic acids are named in the same way.

Natriumbenzoat, benzoesaures Natrium.
Äthylbenzoat, benzoesaures Äthyl.
Bleistearat, stearinsaures Blei.

* Chlorates may also be named thus:—Kalium chloricum, KClO₃. This terminology causes confusion of chlorates with chlorides, even among Germans.

(3). Acid salts are distinguished as follows:—

(normales) Natriumkarbonat, kohlsaures	
Natrium	Na_2CO_3
primäres Natriumkarbonat	} NaHCO_3
saures Natriumkarbonat	
saures kohlsaures Natrium	
doppeltkohlsaures Natrium	
Natriumbikarbonat	
normales, secundäres, primäres Natriumphosphat,	
Na_3PO_4 , Na_2HPO_4 , NaH_2PO_4 .	

Cyanogen Compounds.

Cyan	(CN) ₂
Cyanwasserstoff	} HCN
Cyanwasserstoffsäure	
Cyankalium	KCN
Cyansäure	HCNO
Kaliumeisencyanür	$\text{K}_4\text{Fe}(\text{CN})_6$
Kaliumeisencyanid	$\text{K}_3\text{Fe}(\text{CN})_6$
Ferrocyanwasserstoff	} $\text{H}_4\text{Fe}(\text{CN})_6$
Ferrocyanwasserstoffsäure	
Schwefelcyansäure	} HCNS
Thiocyansäure	
Rhodanwasserstoff	
Rhodanwasserstoffsäure	
Rhodansäure	} KCNS
Rhodankalium, Kaliumrhodanid	
Eisnerhodanür	$\text{Fe}(\text{CNS})_2$
Eisnerhodanid	$\text{Fe}_2(\text{CNS})_6$

There are further, as in English, a large number of non-systematic names, of ancient and popular origin, some of which may not be found in ordinary dictionaries. Under this heading come almost all names of organic compounds which are not readily understood by anyone familiar with their English equivalents. A few names of reagents, &c., are also given below, but no attempt is made to give the very numerous names of ores and minerals.

Ameisensäure	Formic Acid
Äpfelsäure	Malic Acid
Ätz- (in compounds)	Caustic
Atzkali, -natron, -baryt	Caustic potash, Caustic soda, Baryta
Äther	Ether, also Ester
Berlinerblau	Prussian Blue
Bernsteinsäure	Succinic Acid
Bimstein	Pumice
Bittermandelöl	Benzaldehyde
Bittersalz	Epsom Salts
Blausäure	Prussic Acid
Bleiessig	Basic Lead Acetate
Bleizucker	Lead Acetate
gelbes Blutlaugensalz	Potassium Ferrocyanide
rothes "	" Ferricyanide
Braunstein	Manganese Dioxide
Brechweinstein	Tartar Emetic
Brennspiritus	Methylated Spirit
Brenz- (in compounds)	pyro-
e.g., Brenzcatechin,	
Brenzschleimsäure	
Buttersäure	Butyric Acid
Chamäleonlösung	Potassium Permanganate solution
Chlorkalk	Bleaching Powder
Curcuma	Turmeric
Eisessig	Glacial Acetic Acid
Essigsäure	Acetic Acid
Flussäure	Commercial Hydrofluoric Acid
Gallussäure	Gallic Acid
Gerbsäure	Tannic Acid
Gips	Gypsum
Grubengas	Marsh gas
Harnsäure	Uric Acid

Harnstoff	Urea
Höllenstein	Silver Nitrate
Holzgeist	Wood Spirit
Kali	Caustic Potash; also used in place of Kalium in names of potassium compounds
Kalk, gebrannter Kalk	Quicklime
Kalkhydrat, gelöschter Kalk	Slaked Lime
Kieselerde	Silica
Knallgas	explosive mixture of Hydrogen and Oxygen
Knallquecksilber	Fulminate of Mercury
Knallsäure	Fulminic Acid
Kochsalz	Sodium Chloride
Königswasser	Aqua Regia
Lachgas	Laughing Gas
Lakmus	Litmus
Leuchtgas	Coal-gas
Mennige	Triplumbic Tetroxide
Milchsäure	Lactic Acid
Natron	Caustic Soda; also used in place of Natrium in names of sodium compounds
Natronkalk	Soda Lime
Ölsäure	Oleic Acid
Phosphorsalz	Microcosmic Salt
Pottasche	Potassium Carbonate
Salmiak	Ammonium Chloride
Salmiakgeist	commercial Ammonia
Salpeter	Potassium Nitrate
Salpetersäure	Nitric Acid
Salzsäure	Hydrochloric Acid
Schlagvetter	Fire-damp
Schleimsäure	Mucic Acid
Seignettesalz	Rochelle Salt
Senföl	Oil of Mustard
Sumpfgas	Marsh gas
Traubensäure	Racemic Acid
Weinsäure	Tartaric Acid
Antiweinsäure	Mesotartaric Acid
Weingeist	Spirits of Wine
Zimtsäure	Cinnamic Acid
Zitronensäure	Citric Acid
Zucker—	
Frucht-	Levulose
Malz-	Maltose
Milch-	Lactose
Rohr-	Cane-sugar
Trauben-	Dextrose
Zuckersäure	Saccharic Acid

Royal Society Register of Scientific and Technical Men in connection with the War.—The Royal Society is compiling a register of scientific and technical men in Great Britain and Ireland who are willing to give their services in connection with the war. The register is classified into subjects, and will ultimately constitute a large panel of men of standing whose services will be available whenever any Government Department or similar authority requires specialist assistance. The register is being co-ordinated with those independently compiled by other societies and institutions, but the Royal Society would be glad to have applications for forms from such members of the staffs of colleges and technical institutions as have not yet been registered by any society. The Royal Society is also drawing up, with the co-operation of the principal societies and institutions, a list of scientific and technical men actually on active service in His Majesty's forces. Any names, with rank and unit, for this list will be gratefully received by the Secretaries at Burlington House. The task of forming this register has been much facilitated by the assistance of many universities, university colleges, and scientific societies, whose help the Royal Society gratefully acknowledges.

MASS, WEIGHT, AND ELECTRICAL INERTIA.

SOME FURTHER REMARKS.

By F. H. LORING.

MR. H. STANLEY REDGROVE'S further communication on the subject of matter, mass, and weight in the *CHEMICAL NEWS* (cxii., 64), in which he justifies his point of view as distinguished from mine (*CHEMICAL NEWS*, cxii., 37) raises some questions which require clearing up from my standpoint.

If I may be allowed to usurp a little more valuable space in discussing this topic, which should be of general interest, I will partly traverse the statement made by Mr. Redgrove at the end of the first paragraph of his latter communication, and add some comments and quotations bearing on the subject.

Without multiplying examples, we know that 1 grm. of oxygen by weight has half the inertia of 2 grms. of oxygen by weight, and therefore we are justified in assuming that the inertias are equal to the quantities of matter, and the quantities of matter are equal to the masses, or, rather *are* the masses, since we define quantity of matter thus:—"Quantity of Matter. *Mch.*, mass as measured by the product of volume and density."

When, however, we come to define quantity of matter in terms of positive and negative electrons, that is to say, by their numbers, we are involved in two principal difficulties. In the first place, we do not know whether the positive electron is the hydrogen atom divorced from its negative charge (negative electron), and in the second place we do not know whether the sum of n hydrogen-electrons is equal to n corresponding inertias, because it is suspected that in the building-up of the elements (atoms) from primary units in the fundamental manner implied, a change in weight and mass is involved, due to the interaction of electric or electromagnetic fields, so that, for example, $4 \times 1.0078 = 4.0312$, but we are here introducing purely speculative ideas (see *CHEMICAL NEWS*, cx., 26, end of article). The negative electron plays some electrical part in the atom, but we can neglect it for the moment as a direct weight-giving body, because we do not know whether it has weight, and, moreover, whether it even augments the mass of the atom by a very appreciable amount. We must bear in mind that a free electron of necessity has a minute field round it which might be described as a stray field, as distinguished from the relatively more confined or bound-up field (lines of force) such as would result from its comparatively close proximity to a positive nucleus or core; that is to say, when it forms a part of the atomic system. This may make a difference. It takes a very powerful magnetic field to deflect a moving atom of hydrogen (see positive-ray experiments), whereas a weak field will deflect a moving electron, but I may be wrong in implying that this difference is due in part to the configuration of the moving field.

Thus it will be seen that the definition of matter in a quantitative or additive sense involves a number of connected considerations that become interdependent, and therefore the definition of mass as quantity of matter is in reality only a statement that brings our ideas to a material starting point which is the result or basis of general experience. We cannot properly experience mechanical inertia without handling masses of matter. The initial definition of mass I chose, as being a sort of anchor to earth, was merely an apportionment of matter so that it could be handled in the following sense:—"If we have a given amount of matter in the volume-density sense we shall know the force needed to move it, &c.† It is true

that the expression *quantity of matter* is not derived independently of mass or weight, but when more is known of the atom we may be able to define quantity of matter statistically in atomic and (or) sub-atomic units.

Such an expression as "extended substance," in my opinion, means nothing, since it is impossible to say where the extension is going to stop. It may have meant something at the time when the whole cosmic universe was one extension of mist-like substance or continuum (granting this supposition). I prefer to look upwards and note the vast spaces *between* stars, and think of matter as Sir William Crookes pictured it; as having condensed into these forms, since what is true of the stellar universe is perhaps true of the atomic universe, or *vice versa*. The atoms appear to be condensations or accretions of at least positive and negative electrons. There may be something else.

The phenomenon of electrical inertia is of fundamental significance, and Mr. Redgrove may be right in the long run (if I may so express it), though I prefer to keep apart ideas so widely separated by experience and to think of two kinds of inertias or masses, as it were. I agree with Mr. Redgrove in so far that there are not two kinds of inertia *as such*, but these terms are meaningless to me by themselves in practical considerations. When we say *electromagnetic mass*, for example, we mean mass of electromagnetic origin, and we have to consider what this means and that with which it is associated (namely, electrons), otherwise the term is unintelligible. Similarly, when we speak of the mass of a grm. standard, we have to consider that we are dealing with *ponderable matter* under certain specified conditions. Or, to put it another way, it is better, in my opinion, to think in terms of experiment.

It may not be amiss to attempt (provisionally in part) a definition of electrical inertia. I would define it as that property of *electricity*, considered apart from ponderable matter, by which it tends when at rest to remain so, and when in motion to continue in motion. . . . This is an adaptation in part of the definition of the word *inertia* in "Webster's Dictionary," 1911. Continuing, *electromagnetic mass* is a particular phase or aspect of electrical inertia, involving in the case under consideration electronic motion, since an electromagnetic field (as distinguished from an electrostatic field) is engendered by moving charges of electricity, the charge at rest being electrostatic, as the name implies. Hence we come to think of the mass of

* We do not say from an experimental point of view that *mechanical energy* is the same thing (identical with) *electrical energy*, though both degrade into, or may be dissipated as, *heat*. Therefore we should not say that *mechanical inertia* is the same thing as *electrical inertia*; that is to say, they are not identifiable as circumstantial variations of the same phenomenon, unless we assume that electricity and matter are one and the same—which has not yet been proved.

We cannot say a sponge is water because it *holds* water, yet if the sponge itself when analysed had only hydrogen and oxygen, then we might from Mr. Redgrove's point of view be justified in saying that both were circumstantial variations of the same phenomenon; and, going back to the energy problem, since both energies give rise to heat, they too, then, are seemingly circumstantial variations of one phenomenon, therefore "inertia is inertia" as Mr. Redgrove says (see his original statement), and I agree, if it be permissible to make the "circumstantial variation" so wide in its meaning as to include in its range practically all phenomena.

Mr. Redgrove's statement that there is nothing more in a phenomenon than its appearance is most illuminating when we adopt the relativity point of view, which involves a species of logic in my opinion. We then think of *time* and *space* as phenomena which are as much a part or condition of any physical process (phenomenon) as anything else, and we can even begin to see why the mind cannot consistently conceive the end of space, or the beginning of things, but this is more a philosophy that reduces all conceptions to an abstract scale (in the sense, for example, that there is no such thing as a *real* length, either of time or space) than a system of mechanics based upon common experience directly interpreted.

It seems to me that these relativistic and quantistic ideas (see quotation at close of this article) cannot be clearly comprehended until a complete new system of terminology is devised, which may, indeed, involve a modification of mathematical concepts all round. If we can, for instance, *substantialise* (if I may use this term in special sense) mathematics, then we can use such a system to prove the abstractness or unsubstantialness of phenomena. At present it is the other way about, except for such work as Minkowski's, for example, which seems to be along some such lines.

† This quotation is from "Webster's Dictionary," 1911.
‡ "Mass, *Physics*. The measure or expression of quantity of matter in a body as indicated either by its weight or by the amount of force necessary to produce a given amount of motion in the body in a given time."—"New Standard Dictionary" (1914). "Mass, *Physics*. The quantity of matter which a body contains; in strict use distinguished from *weight*, though the two terms are often used indiscriminately."—"New English Dictionary" (1908), Oxford.

an electron as having an electromagnetic origin, since it is only observable when the electron is set in motion. The electron as studied in the vacuum-tube tends to persist (or persists) in a straight line when projected (under an E.M.F.) unless acted upon laterally by either electrostatic or electromagnetic forces (fields) or both conjointly.

That the old mechanics or the ordinary laws of motion are still recognised by advanced thinkers and experimentalists, and that they play a part in radio-physics is evinced by the following quotation from Sir Ernest Rutherford's Royal Institution Lecture, reported in *Engineering* of June 11, 1915, p. 657:—"The α -particle [helium atom of atomic mass=4, with two associated positive charges of electricity as we express it] being expelled from the radio-active atom at a very high speed, the residue left recoiled as a gun did when fired. By similar means to those already explained it was possible to find the velocity of this recoil, which was sufficient to carry the atom back through some centimetres of air at 1 mm. pressure. If the ordinary laws of mechanics held for these atomic explosions the momentum of the recoiling mass should be equal to that of the α -particle expelled, and this was found by Makower to be the case. It appeared, however, that the recoil-atom carried one charge only. Since the momentum of the recoil-atom was the same as that of the α -particle expelled, it appeared that the ordinary principles of mechanics still held, even for these exceedingly violent atomic explosions."

The velocity in this case is not of course equal to that of high-speed electrons (β -particles), but we may never be able to attain with matter a speed approaching closely that of light. If there is such a speed-limit it seems to me that the Newtonian system of mechanics is absolute.

I do not know how far Mr. Redgrove has been influenced by the modern relativity and quantum ideas, but these, quite apart from practical Newtonian mechanics, claim consideration, though the latter has been the basis of Celestial mechanics, the accuracy of which has never been questioned.

We must also, in my opinion, reserve judgment as regards the absolute truth of the principle of relativity. I will quote from Prof. Wood's "Physical Optics" (1914, pp. 692-694):—

"In the foregoing treatment an attempt has been made to give an idea of how the principle of relativity is applied in the case of measurements of the velocity of light. In spite of what has been said about setting systems in motion, it must be clearly understood that absolute motion plays no part at all in the theory. There is nothing to distinguish the motion of a system past an observer from his motion past the system, and the physical phenomena will appear the same in each case. There are applications of the theory much wider than any that have been taken up in this very elementary treatment. Especially interesting are the conclusions regarding the apparent 'mass' of radiation. If we have a body, isolated in space, which is emitting radiation in a single direction, the 'recoil pressure' of radiation will exert a force which we should imagine would give to the body an absolute motion. If E is the amount of energy emitted per second, this force will be E/c . On the principle of relativity there can be no absolute motion, and we are forced to the conclusion that the radiation must possess mass, and carry away a portion of the total mass with it. If we call M the mass of the radiation, its momentum is Mc , which must be equal to the force exerted on the system. We have then $E/c = Mc$, or $M = E/c^2$, from which it follows that we must regard a portion of the mass as represented by the energy contained in a substance. [In this connection see CHEM. NEWS, cxi., p. 157]. The liberation of energy should be accompanied by a reduction in the mass (as measured by its inertia). Whether a change in weight would result is uncertain, for we cannot be sure that inertia and weight are proportional under all circumstances. Einstein [the inventor of this modern relativity] suggests that the vast liberation of energy

which accompanies radio-active changes may enable us to detect the change in mass. [Experiments recently tried give negative results. See Thomson's "Atomic Theory."] It is possible that the theory of relativity will reawaken an interest in the old question of whether a change of weight results from chemical action, or any change of state which involves the liberation or absorption of a large amount of energy. [Recent experiments give negative results]. Einstein even goes so far as to suggest that the radiation is something that is expelled as definite units which move out without loss of energy. This means, of course, that the energy is not equally distributed over what we have been accustomed to speak of as the wave-front, but is localised at points [see Report cited below, p. 87]. Planck has come to the conclusion, from a different line of reasoning, that energy is liberated or absorbed only in units (*Lichtquanten*), but does not believe in the discontinuities in the energy distribution over the wave-front. [See "Report on Radiation and the Quantum Theory," 1914, by Jeans—"The Electrician" Printing and Publishing Company. The treatment is largely mathematical]. He draws attention to the circumstance that interference with a large path-difference shows that the units of radiation must be regarded as having lengths equal to many thousand wave-lengths."

The following may be of interest in connection with these obscure matters:—If we imagine a point-cube, one side of which is continuously projected off flatwise into space we have a line which we might specify as a force-line. This really involves three dimensions. If we now imagine a point-sphere (a sphere being an absolutely symmetrical figure of revolution on every axis, with an infinite number of facets), a similar continuous projection of a portion of its surface, say a sixth part of its superficial area, would result in an expanding volume figure, and if we consider the angle subtended as a sort of "fourth dimension," we have a picture of a volume element as distinguished from the line element. This idea applied to radiation brings it very near to that of primary matter taken as "extended substance" (see above—see below.) Continuing the quotation—

"The principle of relativity has been subjected to experimental tests, with good results, by Kaufmann and Bucherer, who have studied the laws which govern the motions of the electrons which constitute the β -rays of radium and travel at velocities of the same order of magnitude as that of light. [Cunningham, in his "Principle of Relativity," 1914, Cambridge University Press, discussing the dynamics of the electron, gives on pp. 151-153 a summary of the e/m experimental values found for β -particles by several investigators, and this forms perhaps the main pillar upon which this theory of relativity rests. The concordance of these results under mathematical interpretation is certainly remarkable]. The reader is referred to the original papers of Einstein (*Annalen der Physik*, 1905, 1907) and Minkowski (*Phys. Zeitschr.*, 1909, x., p. 104) for the complete mathematical treatment. Minkowski adopts a novel method of showing the space and time relations. To the three axes of co-ordinates, x , y , and z , he adds a fourth, the time-axis. Time thus becomes the fourth dimension [see Wells' novel], and the transformation equations correspond to a rotation of the four-dimensional reference system

x, y, z, ict through the imaginary angle $\arctan \left(\frac{v}{c} \right)$.

Minkowski starts out with the statement that we only observe a place at a given time, and time at a given place. Space and time are thus bound together, and a time-axis

* I will here quote a few lines from Wells' "Time Machine." Introduction: "Can an instantaneous cube exist?" "Can a cube that does not last for any time at all have a real existence?" "Clearly, any real body must have extension in four directions: it must have Length, Breadth, Thickness, and—Duration." "There is no difference between Time and any of the three dimensions of Space except that our consciousness moves along with it."

is added to the co-ordinate system. This brings us at once into non-Euclidian geometry, for the time-axis runs in a direction perpendicular to all three of the directions x , y , and z , of our space co-ordinate system. We cannot, of course, conceive this direction at all, except perhaps in a vague way by the methods given in the popular articles on the fourth dimension."

I appreciate Mr. Redgrove's considerate remarks. I prefer, however, to adhere to my points of view.

THE VAPOUR PRESSURE OF CONCENTRATED SUGAR SOLUTIONS.*

By D. ORSON WOOD, B.Sc., A.R.C.Sc.

(Continued from p. 94),

Results.

IN order to determine the probable degree of accuracy that would be obtained from the method, an experiment was made with water instead of a solution. The results are given at some length in Table I., so that the magnitude of the various corrections involved may be exhibited.

TABLE I.—The Vapour Pressure of Pure Water.

Thermo- meter reading.	Emer- gent stem correction.	Temperature corrected for stem and thermo- meter.	Ob- served pressure.	Pressure reduced to cm. mer- cury at 0° C.	Pressure cor- rected for columns.
°C.	°C.	°C.	Cm.	°C.	Cm.
58.49	—	58.49	13.93	13.89	13.84
62.37	0.02	62.35	16.69	16.63	16.58
65.21	0.03	65.19	18.09	18.03	18.87
68.70	0.05	68.68	22.10	22.02	21.96
72.14	0.06	72.13	25.63	25.54	25.47
77.27	0.11	77.32	31.89	31.77	31.70
80.00	0.15	80.14	35.76	35.64	35.56
84.66	0.20	84.91	43.15	42.99	42.91
88.85	0.22	89.04	50.63	50.45	50.36

TABLE II.—The Vapour Pressure of Water.

Tem- perature. °C.	Value from curve.	Regnault.	Landolt and Börnstein's tab. es.	Dif- ference. Cm.	Dif- ference. °C.
60	14.86	14.88	14.92	0.06	0.07
65	18.69	18.71	18.75	0.06	0.07
70	23.28	23.31	23.38	0.10	0.10
75	28.75	28.88	28.93	0.18	0.15
80	35.38	35.46	35.55	0.17	0.12
85	43.10	43.32	43.38	0.28	0.16
90	52.30	52.55	52.60	0.30	0.15

These results were plotted on a large scale, and a smooth curve was drawn through the points. This curve is parallel to, but a little to the right of, that obtained by plotting the standard values of the vapour pressure. The vapour pressure for each 5° above 60° C. was read off from the experimental curve, and the numbers so obtained are shown in Table II.

The values given by the experiment are all too small, so that there is no evidence of the presence of dissolved air. The difference is possibly due to impurity in the water used, and, in this connection, it must be pointed out that, during the filling process, the water may become contaminated with grease. No traces of this, however, were ever visible in the solutions, and it does not necessarily follow that the grease would decrease the vapour pressure; its effect might go the other way. The degree of accuracy shown in these results—rather better than one part in two hundred—is sufficient for most of the purposes of this paper, the more especially as it indicates that the observed pressures are probably too low.

Experiments were carried out with three solutions, referred to hereafter as I., II., and III. They contained

approximately 48, 61, and 69 grms. of saccharose to 100 grms. of solution. Their exact concentrations expressed in the different units in common use are shown in Table III.

TABLE III.—The Concentration of the Solutions.

	Solution No. I.	Solution No. II.	Solution No. III.
Grms. of sugar per 100 grms. of solution	47.97	61.02	69.20
Grms. of sugar per litre of solution at 20° C.	585	789	928
Grms. of sugar per 100 grms. of water	92.0	156.6	224.3
$n/N = \frac{\text{gram. molecules of sugar}}{\text{gram. molecules of water}}$	0.0486	0.0824	0.1182

TABLE IV.

T °C.	π_{π} .	$\frac{\pi_0 - \pi_{\pi}}{\pi_0}$.
Solution I.		
60.42	14.60	0.041
63.39	16.58	0.048
66.02	18.47	0.057
72.95	24.78	0.065
74.23	26.25	0.062
80.42	34.49	0.045
82.78	37.39	0.058
84.86	40.10	0.070
90.00	49.60	0.057
Solution II.		
62.98	15.18	0.112
67.51	18.69	0.108
73.08	23.75	0.109
78.55	29.86	0.106
83.35	36.38	0.104
87.61	42.93	0.106
90.85	48.58	0.107
[92.66	52.71	0.093]
Solution III.		
59.0	11.27	0.208
62.9	13.60	0.203
68.2	17.37	0.196
73.9	22.25	0.194
75.1	23.50	0.191
78.8	27.68	0.183
84.9	35.94	0.169
89.1	41.64	0.181
92.0	46.44	0.181

π_0 = vapour pressure of water under its own vapour pressure, taken from Landolt.

π_{π} = vapour pressure of solution under its own vapour pressure.

The first successful experiment was made with 69 per cent solution. In this experiment only hand stirring of the water-bath was possible, while, in every other case, a mechanical stirrer was used. In consequence, the temperatures read in this experiment are only given here to the nearest tenth of a degree. In order to check the concentration, and, in particular, to see that it had not increased owing to evaporation during the filling process, the density of the solution was determined at the end of the experiment. According to this determination the concentration was 69.8 per cent instead of 69.2 per cent; as good an agreement as could be expected, and, as the density method was only regarded as a check on the other, the strength calculated from the masses of the sugar and solution at the commencement of the experiment was taken to be correct. It is important to notice that this concentration, if in error at all, will be too small.

The measurements of the vapour pressures of Solution I. were evidently less satisfactory than the others, because the points, when plotted, did not lie well on the curve drawn through them. In consequence less stress can be laid on the depression of vapour pressure calculated from these results than in the other cases.

* A Paper read before the Faraday Society, May 11, 1915.

Table IV. gives the result of the observations. Each vapour pressure given in that table is the mean of a number of determinations (varying from three to eight) taken at approximately the same temperature; i.e., within 0.5° C. These observations were plotted on a very large scale, and a weighed mean was calculated. The lowering of vapour pressure relative to the vapour pressure of water is shown also, but the values on which the following discussion is based were obtained from large-scale curves plotted from the data given in this table. It will be seen at once that the variation of Babo's constant with temperature is quite small even for such syrupy solutions as are being dealt with here.

Discussion of Results.

The value of the measurements can best be gauged by using them to calculate the heat of dilution of the solutions, and this, therefore, is given first; subsequently, they are discussed from the point of view of the theory of solution and of osmotic pressure.

The latent heat of dilution is the heat that must be added to a (theoretically) infinite amount of solution in order to keep its temperature constant when 1 grm. of the solvent is added to it. Defined in this way it is positive when adiabatic dilution is accompanied by cooling.

It will be sufficient for the present argument to assume the well-known Kirchhoff equation, which gives for the latent heat—

$$H = RT \cdot \frac{\partial}{\partial T} \left(\log_e \frac{\pi_0}{\pi_\pi} \right),$$

where R, the gas constant for water vapour, varies inversely as the molecular weight of the vapour. It follows, then, that, leaving out of consideration any possible change R may undergo with rise of temperature, the smaller H may be the less should be the variation of $\log \pi_0/\pi_\pi$. Moreover, if H is positive, this expression should increase with rise of temperature, and if H is negative, so that the solution warms when diluted adiabatically, it should decrease. Table V. shows the values of the logarithm of the ratio for each solution at different temperatures.

TABLE V.
Log₁₀(π_0/π_π).

Temperature. °C.	I.	II.	III.
60	0.0212	0.0536	0.0993
65	0.0221	0.0508	0.0963
70	0.0223	0.0492	0.0944
75	0.0236	0.0504	0.0920
80	0.0229	0.0496	0.0856
85	0.0258	0.0487	0.0827
90	0.0252	0.0480	0.0843

It will be seen that for Solutions II. and III. there is a continuous decrease, while the weakest solution shows an increase with increase of temperature. There do not seem to be many data on latent heats of dilution available. Stackelberg (*Zeit. Phys. Chem.*, 1898, 26) has measured it in a number of cases, but the strongest solution he used contained about 37 grms. of sugar per 100 grms. of water; for this he found the latent heat to be -0.31 calories per grm. at room temperature, while approximately the same value can be calculated from observations by Morse and his collaborators (Moore, Holland, Myers, Cash, and Zinn, *Am. Chem. Journ.*, xlviii., 29) of the temperature variation of the osmotic pressure of a solution of about the same strength. (See the section of this paper dealing with osmotic pressure). The sign of these results corresponds to a decrease in $\log \pi_0/\pi_\pi$ with rise of temperature. A rough experiment (see Note) with a strong solution at 20° C. gave a much larger negative value for H, so that it is probable that the ratio should decrease for all three solutions.

(NOTE.—A solution containing 68.6 grms. of sugar to 100 grms. of solution was prepared. Its specific heat was found to be 0.614. When 87 grms. of it were diluted to 63.6 grms. sugar per 100 grms. solution by adding 6.8 grms. of water the temperature rose 0.20° C., representing a true

rise of 0.18° C. when radiation was allowed for. This gives H of the order -2 calories per grm. at 20° C.).

The actual value of the heat of dilution at 60° C. (not 20° C.) calculated from the vapour pressure measurements by means of Kirchhoff's equation is -5.26 cal./grm. for Solution II. and -14.03 cal./grm. for Solution III.

(Porter, *Trans. Faraday Soc.*, has shown that a more accurate expression is—

$$H = T^2 \frac{\partial}{\partial T} \left\{ RT \log_e \frac{\pi_0}{\pi_\pi} - \frac{c(\pi_0 - \pi_\pi)}{T} \right\},$$

where c is the "coaggregation factor" in Callendar's gas equation. This equation gives H = -5.52 cal./grm. for Solution II. and -14.7 cal./grm. for Solution III. at 60° C. The second term being about 5 per cent of the first, which is, of course, Kirchhoff's expression).

These values are very large, much larger than the 2 cal./grm. obtained by experiment for solutions of about the same strength, so that the variation of $\log \pi_0/\pi_\pi$ shown by direct measurement is almost certainly too large.

If $\log \pi_0/\pi_\pi$ is plotted against temperature the majority of the points appear to lie on a straight line. If this be correct $\frac{\partial}{\partial T} \left(\log \frac{\pi_0}{\pi_\pi} \right)$ is constant, and the latent

heat of dilution should be proportional to the square of the absolute temperature within the limits to which Kirchhoff's equation applies. Magie (*Phys. Rev.*, 1912, 35) has made experiments on several solutes over a range from 3° C. to 27° C., which verify a linear formula due to Thomsen. A calorimeter has been constructed with which it is hoped that measurements may be made over a large range of temperature, so that accurate values of the dilution heat and its variation may be available to test the vapour pressure results.

The measurements made by Perman and Price (*Trans. Faraday Soc.*, 8) at 70° C. and 90° C. with several concentrations, show in every case an increase of $\log_{10} \pi_0/\pi_\pi$ with rise of temperature. Thus, for a solution containing 9.2 grm. molecules of saccharose to 100 grm. molecules of water, their data give for this expression 0.040 at 70° C. and 0.056 at 90° C., an increase of 30 per cent, the corresponding value of the latent heat of dilution which can be calculated from this being +25 cal./grm. This means that, according to their observations, there should be a considerable cooling instead of warming when the solution is diluted with water under adiabatic conditions. On the other hand, experimenting with calcium chloride they obtained a small decrease in the ratio with rise of temperature. (E.g., a solution containing 12 grm. molecules of salt per 100 of water gave $\log_{10} \pi_0/\pi_\pi = 0.384$ at 70° C. and 0.358 at 90° C.—a decrease of 6.5 per cent). This again gives a dilution heat of the wrong sign (see, for example, Stackelberg, *loc. cit.*). These figures are sufficient to show that results calculated from air current data are subject to errors which become of serious consequence when the depression of the vapour pressure is required.

(To be continued)

The Glass of Rheims Cathedral.—An interesting study of the mediæval glass from the windows of Rheims Cathedral has, says *Knowledge*, been made by M. G. Chesneau. He finds that violet glass contains iron oxide and traces of copper and cobalt, in addition to manganese. The presence of these elements points to the use of impure pyrolusites in the manufacture of the glass. The blue glass contains the elements usually found in association in native arsenio-sulphide of cobalt. The absence of any nickel in the glass indicates that means had been discovered in the thirteenth century of excluding it from zaffre, and thus preventing the brown coloration produced by nickel. The green glass contains the mixed oxides of copper and iron, together with a small amount of cobalt and a large amount of manganese. The red glass appears to have been produced by means of a very thin layer of enamel, which was coloured with cuprous oxide.—*Knowledge*.

CHEMICAL ENGINEERING.*

By G. T. BEILBY, D.Sc., F.R.S.

ONE of the lessons of the critical times through which we are passing is that as a nation we are lacking in organisation. I fear it must be admitted that even our capacity for organisation is still undeveloped. With our usual frankness in the discussion of our national defects we have sometimes made it appear as if we actually enjoyed this outspoken self-depreciation, but there are unfortunately signs that our zeal for discussion may spend itself without leading us any further towards reform. As a Society of industrial chemists it is our duty to see to it that this fatal arrest in the pathway of reform shall not occur. The discussion this afternoon is to turn not on any of the wider aspects of the national organisation of Industry, but on certain more domestic questions of organisation within the individual works. We may take it, I think, that the President and Council in preparing the programme of this annual meeting have recognised the deep significance of the present situation. Though I was specifically invited to open a discussion on Chemical Engineering I shall take the liberty of treating the subject as a central feature in works' organisation rather than as a subject by itself.

Chemical engineering was first introduced as a subject for discussion by the Society in an address to the London Section in 1899, and since then a good deal has been said and written on the subject. It now finds an honoured place in the curricula of several of the leading colleges, and it is recognised as a subject for a degree by one or more of our universities. Chemical engineering has therefore taken its place as a subject for professional study, and I gladly spare you any reiterated arguments in its favour.

Inasmuch as all works of construction involve questions of engineering, we may take it that even the more crudely equipped chemical works have required for their construction a certain amount of engineering skill. Buildings have had to be erected, drainage and water supply provided for, and prime movers installed. Provision has had to be made for the evaporation or distillation of liquids under augmented or diminished pressure, for the condensation and fractionation of vapours, and for the cooling, filtration, and crystallisation of solutions. There is not one of these operations which had not been systematically carried out on a large scale long before chemical engineering had been accepted as a special branch of professional study and practice. In the development of processes on a large scale improved mechanical appliances have always played an important part, and early in the day engineering firms in chemical manufacturing districts specialised in the manufacture of these appliances. But these firms had not found it necessary to maintain their own chemical laboratories or to employ chemical specialists to aid them in their work; they trusted simply to the knowledge and experience obtained at second hand from the chemical manufacturer and his staff.

From these facts it is evident that engineering has always had a definite place in chemical manufacturing, but if we inquire a little more closely into the degree and kind of engineering skill which found a place in the older chemical works, we shall find that it was frequently not of a very high order.

One of the special features of large scale chemical apparatus is the heavy depreciation to which it is subject, and the need, therefore, for continual renewals and repairs. This wear and tear is not simply the result of exposure to atmospheric and other natural agencies, but is due also to the action of the chemical elements and compounds in their most potent forms. The oxidation and burning out of metal and other vessels in high temperature furnaces is a prolific cause of excessive depreciation. The skilled

engineer who has been accustomed to the construction of high-class prime movers or mill machinery may be very ill fitted to design and keep in repair the short-lived apparatus of the chemical works. A more adaptable but rougher type man is required, and these needs have produced a rather special kind of man, the "chemical works engineer" rather than the "chemical engineer." If these facts are kept in mind we shall not find it at all surprising that chemical works plant, especially in the older works, often has an improvised appearance which suggests, either that the engineer in charge is actually slovenly, or that he knows so well the temporary character of the work that he does not think it worth while to conform to the ordinary decencies of engineering design and construction! Tumble-down apparatus is only too apt to react on the processes which are carried on in it, and slipshod working is the outcome. The moral effect of rapid destruction of plant is certainly bad; hence the enlightened manufacturer is willing to make many sacrifices to secure more enduring forms of plant.

Apart from the special characters which are due to the necessity for frequent renewal, there is no doubt that the influence of the chemist has had a definite effect on the design of chemical plant. A former colleague of my own, who had himself made splendid contributions to the improvements of the apparatus used in one particular industry, could find no more contemptuous way of expressing his opinion of any piece of apparatus of which he did not approve than to call it a "chemist job." Of course the chemist did sometimes get back on the engineer if an elaborately designed piece of apparatus failed to give satisfactory results from a process point of view! In this case, unfortunately, any attempt at a *tu quoque* was more than ordinarily ineffective, as an "engineer's job" was just the kind of job the constructor desired to make! It is not easy to define or characterise these two kinds of job by any simple definition. Chemists' apparatus is more the result of opportunism than of deliberately thought-out design. Contingencies are provided for as they arise, and initial mistakes in design are apt to be met in a partial or temporary way. The origin of the chemists' type of apparatus is found in the chemical laboratory, where it has generally been the aim of the professor to develop in his students a certain kind of individual resourcefulness. This resourcefulness is an invaluable possession when pioneering work has to be done. The rapid adaptation of means to end which so naturally results from the properties of the chemists' principal raw material of construction, glass, has given its own definite character to the apparatus of the laboratory. Glass, in the hands of a moderately good glass worker, is a marvellously flexible and adaptable material of construction, and with the help of cork and indiarubber there are few types of chemical apparatus which the chemist cannot easily and quickly fit up for himself. When the chemist needs to increase the scale of his apparatus he naturally follows the type of construction to which he is accustomed, and even when the increased scale gets beyond the resources of the blowpipe table and the cork drawer his ideas flow along the old laboratory lines. When the increase in scale is so considerable that it becomes necessary to call in the help of the engineer and his craftsmen, the designs proposed by the chemist still show their laboratory origin. The quick adaptability of the plumber's methods attract him rather than the engineer's carefully arranged series of steps from the drawing office through the pattern shop, the moulding shed, and the foundry to the machine shop. In pioneering work a "chemist's job" is often the most suitable to use, but when the stage of steady manufacturing has been reached, all the resources of the drawing office and workshops should be devoted to the design and construction of suitable apparatus.

Though there are still many very crudely equipped chemical works in this country, there are others of a more fully developed type which are provided with a properly equipped and staffed drawing office, and mechanical

* Address to the Annual General Meeting of the Members of the Society of Chemical Industry, held at Manchester, July 15th, 1915.

workshops furnished with the most modern machine tools. Reference has already been made to the rapid depreciation of chemical apparatus and to the necessity for frequent repairs and renewals, often of a very radical type. A well designed and built steam engine or other machine often outlives its economic usefulness and escapes scrapping because it still looks as good as new. Chemical plant generally scraps itself, especially if it is allowed to drop out of use even for a short time.

In modern chemical works where sound engineering principles are allowed to have their proper weight, the design of new apparatus is attacked somewhat in the following way. After all process data have been obtained by laboratory methods, the co-operation of the drawing office with the laboratory begins. The nature of each step in the process, and the unit output per hour or per day which is to be adopted, the weight and volume of materials to be dealt with in unit time, the conditions of temperature and pressure required at each stage, the method of assembling the various raw materials and their distribution to the apparatus units, the collection and packing of the finished products, and last but not least, the economical and safe disposal of the waste products, solid, liquid, and gaseous, all these must be collected, sifted, co-ordinated, and discussed, not merely in their own light but also in the light of the most mature experience available among the staff. In addition to the co-operation required to settle the process data, further co-operation is required to find suitable materials for the various parts of the apparatus. These materials may be required to resist the corrosive action of gases and liquids, or the effects of high temperatures or pressures. Sometimes all these adverse influences combined have to be resisted. The materials found suitable by the chemist have to be studied by the craftsmen in the moulding shop, the foundry, the forge, and the machine shop. When the proper materials of construction have been discovered, and the correct methods of handling them have been evolved, the final completion of the designs in the drawing office is a matter of ordinary engineering construction. The completed apparatus ought not only to look like its works, but to do that work with economy and efficiency.

The stage in the evolution of a new process at which this highly organised method of attack on the design of a suitable apparatus ought to be introduced can only be decided for each new problem as it is dealt with. A premature application of the method often leads to loss of time and money. Those who have had any prolonged experience of industrial processes can no doubt call to mind instances of this. Sometimes the study of an apparently well thought-out set of plans may give a fictitious air of reality to a scheme which by right is only in one of the early pioneering stages. The company promoter has been known to realise the financial value of this apparent air of completeness and to turn it to his own account! In spite of these dangers, which ought not to be overlooked, the method of organised attack is the true ideal to be striven after. The great strength of German chemical industry rests on the internal organisation of the works quite as much as on mere abstract research. I use the term abstract research to distinguish this type from the more directly practical inquiries which it has been shown above are a necessary part of an organised attack on a manufacturing problem by the laboratory, the drawing office, and the experimental workshop.

In the modern organisation there is room for the research chemist of high and wide attainments, for the scientifically trained engineer, also of wide attainments, and for a type of professionally trained man who is the natural medium of interchange between these two specialists. This intermediary is the chemical engineer. He must be a man of special aptitudes, inasmuch as *he must have grasped the chemists' point of view as well as the engineers'.* The chemist thinks and works in terms of atoms and molecules and the laws which govern their combination. The engineer thinks of matter in masses

which can be moulded to his will by the craftsman, or of mechanical or electrical energy which can be generated, controlled, and measured by machinery. The chemist is the master and director of his own operations which he can, for the most part, carry out with his own hands. The engineer loses his direct hold on his operations whenever his ideas have been fully committed to paper in the drawing office. It is his special function to organise the labours of many workers. A certain number of men are able to enter fully into the spirit which actuates both types of expert, the chemist and the engineer; they can resist the particular exclusiveness of each, while giving to each its due weight. These are the naturally gifted chemical engineers, who in one sense are "born not made." In our colleges and universities the best that we can do for men of this gifted type is to give them the best possible opportunities for an all-round development of their powers. For the average men we ought to provide a properly organised course of training in theoretical and practical chemistry, physics, and mechanics, on professional, not on purely academic lines. Our colleges have thus two distinct functions to perform, and it is best that this should be clearly recognised—first, to allow the future leaders in applied science to come naturally to the top during their training, and second, to prepare a large number of well trained professional men for the organisation and development of industry. The ideal for these men must be a professional one. The ideal that "every man in the ranks ought to realise that he carries a Marshal's baton in his knapsack" is as false as it is unpractical, and it will never help the drill sergeant to produce useful soldiers nor the commissioned officer to acquire a sound knowledge of his profession. It is to be feared that the making of practical chemists has suffered severely from a similar fallacy, namely, that all students ought to aim at being pioneers in some branch of their science. Science and industry alike call aloud for *real pioneers*, for without these the highest type of progress cannot be realised. This call, however, cannot be met by the premature stimulation of "originality" in men of very ordinary endowment. The effect of this stimulation is not merely futile, it is positively mischievous, for it raises an ideal which for the ordinary man is quite inappropriate during his preparation for a life of serious practical endeavour. In conclusion, I must repeat the statement of my belief that the phenomenal development of chemical industry in Germany has resulted much more from the large command of chemists and engineers of sound professional training and ability than from the possession also of an even larger supply of research chemists of mediocre ability.

THE ANALYSIS OF PLATINUM.*

By F. MYLIUS and A. MAZZUCHELLI.

(Continued from p. 91).

3. Summary of the Separations.

FROM the mixed solution of the chlorides of the platinum metals the osmium is always driven off as volatile tetroxide by evaporation with nitric acid; it is of no further importance in the analytical treatment of the solution. The detection of the other metals is rendered very difficult owing to the changes to which the solutions of their chlorides are exposed. Hydrolysis, oxidation, reduction, formation of complexes, &c., play a very important part. The ready passage from one state of chlorination to the other often masks the most important characteristics. Thus, for iridium precipitation as black ammonium double chloride is characteristic, but only if a brown solution of tetrachloride is used, while no precipitate appears in the yellow solution of the trichloride. It is also known that

* *Zeitschrift für Analytische Chemie*, lxxxix., 1.

palladium, which normally (as dichloride) is not precipitated by ammonium chloride, is precipitated with the ammonium chloride compounds of other platinum metals, if in presence of oxidising agents there is a chance of the formation of palladium tetrachloride.

The increase of the solubility of iridium ammonium chloride by rhodium chloride, &c., may be added to the many examples given in literature.

Ruthenium and its Double Chlorides.—These disturbances of its reactions are perhaps more striking in the case of ruthenium than any other platinum metal; its analytical study is rendered difficult by various unexpected phenomena. For example, the characteristic violet coloration of the ruthenium salts with potassium rhodanide is affected by other platinum metals (*cf.*, Classen, "Ausgew. Methoden, &c.," i., 278). If palladium is precipitated by mercury cyanide the precipitate contains some ruthenium, which would not itself be precipitated. The reduction of metallic platinum by hydrazine hydrochloride is stopped by any ruthenium present according to our observations, &c.

It is specially the ammonium double chlorides which may give rise to many analytical errors, and therefore deserve a further description.

Our ideas concerning the nature of the ammonium double chlorides of ruthenium are not yet quite clear.

The ammonium chloride double salt, $(\text{NH}_4)_2\text{RuCl}_6$, corresponding to ruthenium tetrachloride, is described as a dark red octohedric crystalline powder, the prismatic form of which is similar to, and might be confused with, that of the (readily soluble and not analogous) rhodium salt, $(\text{NH}_4)_2\text{RhCl}_6 \cdot 1\frac{1}{2}\text{H}_2\text{O}$.

On the other hand, an ammonium double chloride of the composition $(\text{NH}_4)_2\text{RuCl}_5$ is said to correspond to ruthenium sesquichloride; it is described as a brown crystalline powder difficultly soluble in water (Claus, *cf.* "Gmelin-Kraut," 3rd Edition, vi., p. 1339). In another place (*loc. cit.*, p. 1324) the difficultly soluble salt is expressly described as the double salt of the sesquichloride. As a hydrochloric acid solution of the sesquioxide hydrate was used and the solutions were evaporated with the addition of nitric acid, there is some justification for doubt whether the observations and analyses have been rightly interpreted.

Recently, to prepare the chlorides it has been found convenient to use distilled per-ruthenic acid, which is dissolved in concentrated hydrochloric acid. According to our observations the original smell of ozone is then replaced by a strong smell of chlorine. The red-brown solution when strongly diluted with water gave, on addition of ammonium chloride, an immediate dark brown difficultly soluble precipitate, which was washed with dilute hydrochloric acid, pressed between filter-paper, and then dried over calcium chloride.

The analysis gave the following result:—

- I. 0.3973 grm. gave 0.9227 AgCl and 0.1195 grm. Ru.
- II. 0.2400 grm. gave 0.0718 grm. Ru.
- III. 0.5505 grm. gave 39.4 cc. N (750 mm., 16.2°).
- IV. 0.1249 grm. gave 0.2927 AgCl.

	Calculated for		Found.				
	$(\text{NH}_4)_2\text{RuCl}_6$	$(\text{NH}_4)_2\text{RuCl}_5$	I.	II.	III.	IV.	V.
	Per cent.	Per cent.					Per cent.
Ru	29.02	32.28	30.1	29.9	—	—	30.0
Cl	60.71	61.15	57.0	—	—	58.0	—
N	7.99	8.89	—	—	8.17	—	—

Analysis V. was performed with material which was obtained from the acid mother-liquor and re-crystallised in presence of free chlorine.

It must be pointed out for the description of the analysed substance that it was almost, but not entirely, soluble in acidified water after drying, giving a brown solution; about 4 per cent. of a dense brown ruthenium oxide remained behind (as the product of hydrolysis during the preparation or drying) which adulterated the double

salt. Seeing that this admixture must raise the percentage of ruthenium a little and lower that of chlorine, there can be no doubt that it is the double salt of ruthenium tetrachloride, $(\text{NH}_4)_2\text{RuCl}_6$, the analogues of which are known for all the platinum metals except rhodium. In external appearance the dark brown octohedric double salt most resembles the black iridium ammonium chloride, but is differentiated from it by its greater solubility and a more decided tendency to undergo hydrolytic decomposition. If the ruthenium chloride is precipitated from its solutions by saturating with ammonium chloride the filtrate always remains a little brownish coloured. The aqueous solution of the difficultly soluble double salt becomes turbid on standing for some time or more quickly on warming, brown hydrated ruthenium oxide being separated. (Red osmium ammonium chloride behaves similarly, for on warming with water it is also decomposed giving brown oxide).

In composition the still more difficultly soluble double salts of potassium, rubidium, and caesium correspond to the difficultly soluble ammonium ruthenium chloride. On the other hand, Gutbier and Zwecker (*Ber.*, xl., i., 690) and Gutbier (*Ber.*, xlv., i., 306) have prepared from ruthenium chloride solutions (1907) a great number of analogous double salts with the chlorides of organic bases, and described them as hexachlororuthenates. All these compounds are derived from ruthenium tetrachloride, which is also capable of combining in solutions with hydrochloric acid to give typical but easily decomposed hydrochlororuthenic acid, H_2RuCl_6 .

We have found that the hydrochloric acid grm.-litre solution of ruthenium prepared from per-ruthenic acid in the course of some weeks loses its power of being precipitated by ammonium chloride, obviously because the free chlorine, which protects the ruthenium tetrachloride from spontaneous decomposition, evaporates. All observations indicate that this compound is of a labile nature, and is spontaneously converted into trichloride, chlorine being split off. The change is completed in a short time on repeated evaporation with hydrochloric acid, and more quickly with the aid of some drops of alcohol. An amorphous residue of an orange-yellow colour is thus obtained; it contains the trichloride (but readily undergoes oxidation and hydrolysis). Its similarly coloured ammonium double chloride is very soluble in water. Thus, there is a distinct parallelism with iridium, the trichloride of which behaves similarly. If rhodium is compared with ruthenium it appears that all the trichlorides of the platinum metals, unlike the tetrachlorides, form readily soluble ammonium double chlorides. Our observations thus contradict the statements of Claus, and also of Gutbier and Trenkel (*Zeit. Anorg. Chem.*, xlv., 166), which we have already quoted, and according to which from ruthenium trichloride brown coloured difficultly soluble ammonium double chlorides are derived.

If chlorine is passed into a yellow solution of ruthenium trichloride a brown coloration appears owing to the formation of tetrachloride, and it acquires the power of being precipitated with ammonium chloride. The brown difficultly soluble double salt also results on the evaporation of a yellow trichloride solution containing ammonium chloride, a property which is exhibited by palladium as well as iridium.

From this discussion it may be seen that from an analytical point of view ruthenium is precipitated from a chloride solution by ammonium chloride only in presence of an oxidising agent which opposes the spontaneous decomposition of the tetrachloride to the trichloride.

If platinum is to be separated from ruthenium it might be successfully done by adding a gentle reducing agent to the solution of the two chlorides and precipitating the platinum with ammonium chloride; the ruthenium should then remain in the mother-liquor as trichloride.

From a practical point of view, however, this anomaly appears which also makes the separation of iridium from platinum impossible. Although ruthenium trichloride is

itself not precipitated by ammonium chloride, the ruthenium salt is partly fixed by the platinum ammonium chloride, the precipitate of which is darkened by it. This also takes place if pure platinum ammonium chloride is suspended in a pure ruthenium trichloride chloride solution; after a short time its yellow colour is changed to a distinct brown. How this absorption of ruthenium, which is possibly dependent upon oxidation, proceeds, we have not further determined, but have only established the fact that the separation of platinum cannot be effected thus.

If other platinum metals are also present, there is still less to be expected from such a method of separating ruthenium. The use of ammonium chloride for ruthenium is, however, of a certain value, inasmuch as it provides a means of precipitating the metal with iridium, from which it can afterwards be separated as volatile tetroxide.

Iridium and Platinum.—To distinguish iridium from platinum it is usually recognised by the black colour of its difficultly soluble ammonium double chloride. In presence of platinum the precipitates are red, and often give rise to confusion with palladium, rhodium, ruthenium, and osmium. In this case there is no better way of characterising iridium than by converting it into the blue dioxide. This excellent reaction has hitherto not been estimated at its true value, because the caustic soda which is recommended as a reagent is not perfectly effectual; the greater part of the iridium tetrachloride is reduced by it to trichloride, soluble in alkali, with formation of sodium hypochlorite. According to our observations a special oxidising agent is necessary to convert the dissolved trichloride into the blue oxide; for this purpose sodium hypochlorite or hypobromite is the best, and hydrogen peroxide is less good. Alkaline iridium solutions are sometimes coloured blue by the oxygen of the air.

(NOTE.—According to Witzmann, "Über die Oxyde des Iridiums," Inaug. Dissertation, Salzungen, 1907) the blue oxide separated by alkaline oxidising agents contains trioxide as well as dioxide).

The reaction was performed as follows:—The much diluted chloride solution was saturated with sodium carbonate till its reaction was faintly alkaline, and first warmed to 100°. (If the warming is omitted the reaction fails). After cooling, a very little faintly alkaline hypochlorite or hypobromite solution is added to the liquid, when the blue dioxide at once separates. In presence of a large excess of platinum coagulation is induced by warming. The reaction allows of the detection with certainty of 0.2 per cent of iridium in the platinum. The blue precipitate can easily be filtered off, but has a tendency to go through the filter blue on long washing with pure water; this can be prevented by adding a small amount of sodium chloride.

In pure dilute platinum chloride solution this reaction gives no precipitate; the blue iridium oxide precipitated from impure platinum solution contains at most a little platinum oxide as the normal reaction product of a stronger action of the alkali. If the reaction is only very faintly alkaline the hydrolysis of the platinum chloride is so inconsiderable that by the hypochlorite reaction small admixtures of platinum in the iridium (mother-liquor of the oxide) can easily be detected.

Other heavy metals (except gold) and the platinum metals are precipitated as oxides. (The black ruthenium oxide would be readily soluble in an excess of hypochlorite, volatile per-ruthenic acid being formed). Thus, in the analysis of impure platinum this reaction can be used for the separation of all metallic impurities (*cf.*, *prox.*).

Platinum, &c., in Iridium.—When it is a question of recognising small quantities of platinum in an iridium chloride solution the colorimetric potassium iodide reaction affords a convenient method. While the dark brown iridium chloride solution is coloured yellow by potassium iodide, yellow platinum chloride solution is coloured red-brown by it. By the darkening of a mixed solution one part of platinum can be plainly detected in 100 parts of iridium. For colorimetric determinations comparison

solutions are prepared by mixing pure iridium and pure platinum solutions which contain 2 to 4 per cent of potassium iodide. It must be remembered, however, that this iodine coloration can be caused not only by platinum but also specially by palladium (and on warming by rhodium also), so that by means of it these impurities can also be easily detected in iridium.

Palladium.—The most characteristic reaction for palladium is precipitation with mercury cyanide, which occurs only with silver amongst the other metals. In presence of a large excess of other platinum metals the reaction is, however, not sensitive enough. They must therefore usually be separated previously with ammonium chloride, while the palladium is kept in solution as dichloride.

Dimethylglyoxime, which has recently been recommended as a reagent (M. Wunder and V. Thüriger, *Zeit. Anal. Chem.*, 1913, lii., 660), loses its applicability very much in presence of other chlorides.

The great velocity of reaction which signalises palladium above the other metals can often be employed advantageously. Even from alloys it can be energetically separated by means of dilute aqua regia. As a second example, the reaction with sulphuretted hydrogen may be mentioned, which instantly causes the separation of a black sulphide, while with the other platinum metals it takes place slowly owing to the formation of soluble intermediate products. This difference can be used for analytical separations.

Palladium can be very quickly and completely precipitated by potassium iodide; the black precipitate is soluble in excess of the precipitant, giving a dark coloration. Finally, we may recall the half-forgotten property of being precipitated with ethylmercaptan. Claesson (*Journ. Prakt. Chem.*, [2], xv., 206), who recommended the use of this preparation in platinum analysis, says (using alcoholic solutions):—"Mercaptan has no action on the lower oxides of the metals iridium, ruthenium, and osmium, and only a reducing action on the higher." For analytical purposes we prefer to use an aqueous 1 per cent solution of mercaptan. By such a solution palladium, platinum, and rhodium, especially on strong acidification with hydrochloric acid, are completely precipitated on warming.

With palladium the precipitation immediately occurs, even in very dilute solutions. Ten cc. of a neutral lower chloride solution, which contains only one hundred-thousandth part of palladium, was immediately coloured yellow by 2 cc. of mercaptan solution: after acidification on warming a dark yellow flocculent precipitate appeared at once, which gave a colourless filtrate. The phenomena were quantitatively analogous when the amount of palladium was only one millionth of the solution.

In chloride solutions of iridium, on the contrary, on gently warming no precipitate appears, which apparently agrees with Claesson's statements. But if the warming with mercaptan and hydrochloric acid (or sodium chloride) is continued for some time a dense precipitate of a light yellow colour slowly appears: it may be regarded as iridium mercaptide, and in its properties it is allied to the other mercaptides of the platinum series. The compound is insoluble in water and in ether, but soluble in warm alcohol. Perhaps this is the reason why it has been overlooked by Claesson.

Similarly, from ruthenium and osmium chloride solutions on warming with mercaptan and hydrochloric acid the mercaptides of these metals separate slowly as dark precipitates which have not been further investigated.

If in accordance with Claesson's suggestion the separation of iridium from platinum or rhodium is attempted by gentle warming of the mixed chloride solutions with mercaptan, much iridium always remains in solution while platinum and rhodium are precipitated, but the mercaptides of these metals are in that case strongly adulterated with iridium mercaptide, so that sharp separations cannot be effected thus.

If ethyl mercaptan is not so valuable for the distinction and separation of the platinum metals as Claesson said, its applicability cannot be entirely denied; but it is limited to the cases in which there is a great difference in the velocity of the reaction, as, for example, in the separation of iridium and platinum, which at room temperature proceeds as satisfactorily with mercaptan as with the analogous sulphuretted hydrogen.

Rhodium.—Except for the rose-red coloration of the chloride solution containing hydrochloric acid or ammonium chloride, rhodium affords only very few specific characteristics from an analytical point of view. On account of its ready solubility the red ammonium double chloride can hardly be regarded as a "precipitate" in analysis, but the difficultly soluble yellow purpureo-rhodium chloride precipitated from ammoniacal solution by the hydrochloric acid is much more to be looked upon as a precipitate, though it may contain iridium; it cannot be used for the separation of very small quantities of rhodium from solutions. Potassium iodide, sulphuretted hydrogen, and mercaptan only precipitate rhodium solutions on warming, unlike palladium solutions.

The luteo cobalt chloride recommended by Gibbs also precipitates rhodium chloride solution containing hydrochloric acid on warming. But sharp analytical separations cannot be effected thus, for other platinum metals besides iridium readily combine with it to give more easily soluble compounds.

Owing to this lack of specific precipitants attempts must be made to concentrate the rhodium as far as possible in the mother-liquor by previously separating the other metals, in order to obtain a colorimetric means of showing its presence, especially of small quantities. The sulphuretted hydrogen reaction can be of great use for this purpose.

If sulphuretted hydrogen is allowed to act at 18° on the dilute solutions of the chlorides of the individual platinum metals the velocity of the reaction follows this order:—Palladium, ruthenium, platinum, rhodium, osmium, iridium. Red rhodium chloride solutions are not altered by sulphuretted hydrogen in a few minutes (like iridium and osmium), while palladium and ruthenium (like copper, lead, gold, &c.) are precipitated. If these metals are present together in a mixed solution, by working quickly an approximate separation can be effected, the first metals being separated, while the rhodium remains in the red filtrate. (It is, however, found that the separated sulphide always contains a trace of rhodium). The rhodium can easily be precipitated as sulphide on warming the filtrate, and determined as metal. But as the original mother-liquor may contain small quantities of other heavy metals precipitated by sulphuretted hydrogen as well as rhodium, and usually does contain them (*e.g.*, Ir, Pt, &c.), the rhodium obtained by igniting the sulphide is rarely quite pure.

Extraction with heated potassium bisulphate, which has often been used as a unique solvent for the metal, is not so effectual as has often been said, and the premature conversion into metal is not always convenient because it prevents the complete separation of the impurities. The precipitated sulphide can, however, be brought into solution by aqua regia. A further purification in the wet way can be attempted with a hydrochloric acid solution of the residue from evaporation.

Silver, Gold, Copper, Iron, &c.—The solutions for analysis are usually chloride solutions which contain other heavy metals in small quantities as well as the platinum metals. In qualitative as well as in quantitative analysis these admixtures must be capable of being detected, which usually presents no very great difficulty. It may, however, be difficult if there are rare impurities of a metallic nature which may not be taken into account in an analytical process. Such a case will not be discussed here.

Silver is separated as silver chloride, gold is extracted with ether as chloride, copper is recognised by the blue colour of its ammoniacal chloride solution, iron by the

yellow colour of the solution of its chloride in hydrochloric acid, nickel, cobalt, &c., by the potassium ferrocyanide reaction.

(To be continued).

PHOTOGRAPHIC SOCIETY'S EXHIBITION.

THE Sixtieth Annual Exhibition of the Royal Photographic Society is now open at the Gallery of the Royal Society of British Artists, Suffolk Street, Pall Mall, and as the Society represents all sections of photographic work the exhibition is appropriately divided into sections covering pictorial, scientific, technical, colour, professional and trade work, and may be described as international in character, notwithstanding the restrictions which the war has placed upon the entries.

The pictorial section occupies the largest of the five rooms, and the two hundred or so photographs comprise portrait studies, landscapes, &c., by most of the best workers, whether members or non-members of the Society. The judges have been catholic in their taste and selection, as we find examples of the most modern impressionistic styles not far removed on the walls from what is sometimes called "straight" photography, by which we understand untouched work, differentiated only from less pictorial photographs by the happiness of selection of subject and suitability of treatment. Even the problem picture is not wanting, as witness some of the works contributed from America.

The often debated question "Is photography an art?" may be more easily answered after a visit to this exhibition, possibly still to the original inclination of the arguer, but it is impossible not to be impressed by the revelation of individuality in the different workers.

The scientific, natural history, and other sections of photographic activity occupy the two rooms at the farther end of the gallery, the walls being densely crowded, and the floors bear the special desks in which are exhibited transparencies both in monochrome and in colour. Very little English astronomical work is to be seen—presumably our home astronomers are otherwise engaged at present—but the American observatories and universities have stepped gallantly into the breach. Among the astronomical exhibits is a series by Father W. F. Rigge, of the Creighton University, showing how a man wrongly accused of murder was proved innocent by the position of a shadow cast by the sun.

In the same section is a remarkable series of photographs dealing with the *empusa fungus*, which affects the house fly and causes its death. The spread of this disease is one of the methods by which scientific men are attempting to rid us of the household pest.

The natural history section is an interesting one, as is to be expected from the inclusion of work by the Brothers Kearton and members of the Nature Society.

Another interesting group of pictures is that entitled "High Speed Photography," in which many athletes appear, many of them now engaged in sterner avocations than sport, and some who have given their lives for the country.

The colour section consists chiefly of Autochrome transparencies, and is not so large as in previous years, nor is the group of photographs in colour upon paper. The judges, however, have found the quality high, and have awarded to one transparency the Society's medal, designed years ago by Wyon.

The professional and trades sections are a revival, having been absent for some years; the latter has been again included at the request of those who find a pleasure in examining the latest triumphs in apparatus at greater leisure than is always possible in a business establishment.

NOTICES OF BOOKS.

Alcoholometric Tables. By Sir EDWARD THORPE, C.B., LL.D., F.R.S. London, New York, Bombay, Calcutta, and Madras: Longmans, Green, and Co. 1915.

THIS book of tables contains in an abbreviated form the article on Alcoholometry in Sir Edward Thorpe's "Dictionary of Applied Chemistry," in which a historical account is given of methods of determining the specific gravity of mixtures of alcohol and water in all proportions and at various temperatures. Explanations are also given of the tables and of the experimental methods employed. The first set of tables, which are exceedingly well printed in bold large type, gives the percentage of alcohol by volume and by weight at 60° F. or 15.6° C. and the percentage of fiscal proof spirit in aqueous solutions of ethyl alcohol of different specific gravities. Table II. shows the indications of Sikes' hydrometer and the percentage of British proof spirit, together with the corresponding percentages of American proof spirit, of ethyl alcohol by weight (Germany), by volume at 15° C. (France), and at 60° F. or 15.6° C. according to Tralles. Table III. gives the indications of Sikes' hydrometer and the percentage of British proof spirit, with the corresponding indications of the hydrometers of Russia, Holland, Spain, and Switzerland.

Fifty-first Annual Report on Alkali, &c., Works. By the CHIEF INSPECTOR. London: Eyre and Spottiswoode, Ltd. 1915.

THIS report, besides containing the usual detailed reports from the various district inspectors with notes and comments by the Chief Inspector, gives a lengthy account of the systematic study of the distillation process at works where zinc ashes (containing volatile chloride) are in use for spelter-making. It was hoped—but the hope was disappointed—that as an outcome of the experience gained an improved form of prolong might be designed, suitable for use under a wide range of conditions. The treatment of the condensation products—pure and skimmings—was also studied and improved methods were suggested.

Certain Standards for Tuberculosis Dispensaries. Harrisburg, Pa.: Wm. Stanley Ray.

THIS pamphlet contains an interesting discussion of the desiderata in the special dispensaries for treating tuberculosis, which have recently been established in Pennsylvania and elsewhere. These dispensaries are indicative of the awakening of the medical profession and of the laity to the serious need for organising a campaign against tuberculosis and for equipping it satisfactorily, and the social aspects of the question are admirably explained. The qualities which should be possessed by the physicians and nurses are discussed, and it is pointed out that the latter have to perform the most important functions of educator and inculcator of principles as well as their more professional duties. The need for the intelligent collecting and classifying of statistics is also emphasised, and the pamphlet should be useful to those who are interested in the treatment of tuberculosis.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxi. No. 1, July 5, 1915.

This number contains no chemical matter.

No. 2, July 12, 1915.

Observations on Malt Amylase.—P. Petit.—Solutions of amylase obtained with pure water or water containing alcohol keep only a short time and contain a large proportion of foreign matter. A solution of diastase which will preserve its activity for several weeks may be made as follows:—Finely powdered malt is infused for twenty-four hours with water containing 30 to 35 per cent of acetone by volume; it is then filtered off and kept in the dark. The diastatic power of the solution was 30 when fresh; it fell to 18 after forty-eight hours and then remained invariable for twenty days. Light causes an increase of acidity and a lowering of diastatic power. The destruction of the diastase is greatly accelerated by the addition of a little eosine. Dry diastase can be obtained by precipitating the infusion with an excess of ether and acetone, allowing to crystallise, and decanting off the clear liquid. A thin layer of matter is thus obtained which may be dried *in vacuo* when yellowish brown scales are obtained. If these are infused in water the aqueous liquid has a strong saccharifying action, though almost the whole of the scaly matter remains undissolved. This aqueous solution is decidedly alkaline to methyl-red, and the addition of substances which diminish its alkalinity; e.g., primary alkaline phosphate, carbon dioxide, increases its activity. The solution liquefies and saccharifies starch to which secondary sodium phosphate has been added, the colour of phenolphthalein being decidedly pink. The substance which is precipitated with acetone and ether and then rapidly infused with water does not give the reaction with guaiacum tincture at once, though it acts normally on starch. The blue coloration is produced slowly, but it appears at once if the solution is aerated. It is not hindered by the presence of formol.

Researches on Glucosidification of Glycerin by α -Glucosidase.—Em. Bourquelot, M. Bridel, and A. Aubry.—The authors have studied the action of α -glucosidase on glycerin, using the same proportions of glycerin, glucose, and water as in their experiments with β -glucosidase. They have not succeeded in isolating the products of synthesis in the crystalline state, but have determined their composition indirectly. After all action was over the water was eliminated by distillation, the excess of glucoside destroyed by fermentation, the glycerin removed by acetone containing one-tenth of its volume of alcohol, the residue dissolved in alcohol and precipitated with acetone. Thus a pasty extract was obtained from which a glucoside product could be isolated. By determining the rotatory power it was found that this product probably consisted of two glucosides the rotatory power of one of which is higher than +129° and that of the other below +120°.

MISCELLANEOUS.

Action of Nitric Acid on Aluminium.—A. Trillat.—Chemically pure nitric acid of maximum concentration has practically no action on 99.5–99.7 per cent aluminium at temperatures below 5°. Between 5° and 30° the action is hardly appreciable even after days; the rapidity of attack increases in proportion to the rise of temperature. As the strength of the acid falls below 40° B. the action increases, being always accelerated by rise of temperature. From the practical point of view the attack of aluminium is very variable according to the circumstances, and hence no fixed rule can be given for its employment. The first requisite of aluminium which is to be in contact with nitric acid is purity. The presence of copper, sodium, or magnesium causes an acceleration of the action, and chlorine and hydrochloric acid have the same effect. Aluminium vessels can be used for the transport of nitric acid of maximum concentration and also for the nitration of cellulose.—*Bulletin de la Société d'Encouragement pour l'Industrie Nationale*, cxxii., No. iii., 455.

THE CHEMICAL NEWS.

VOL. CXII., No. 2910.

(STUDENTS' NUMBER).

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

CANDIDATES for any Degree in this University must either have passed the Matriculation Examination in this University, or be admitted under the Statute which provides that the Senate may admit graduates of or persons who have passed the examinations required for a degree in other Universities approved by it. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, &c., are open to Women upon exactly the same conditions as to Men.

There are three Examinations for Matriculation in each year; commencing on the second Monday in September, January, and June (in 1916 the second Tuesday in June), or July, as may hereafter be determined.

Every Candidate for the Matriculation Examination must apply to the Principal for a Form of Entry on or before August 20, which must be returned fourteen days before the commencement of the September Examination; or must apply for a Form of Entry on or before November 25, which must be returned on or before December 1, for the January Examination; or must apply for a Form of Entry on or before April 25, which must be returned on or before May 1, for the June (or July) Examination; accompanied in each case by the proper Fee, and by a Certificate showing that the Candidate will have completed his Sixteenth Year on or before January 14 for the January Examination, July 31, the end of the Secondary School Year, for the June Examination, and September 15 for the September Examination.

Every candidate entering for the Matriculation Examination must pay a Fee of £2.

Intending Students (Internal and External) should obtain the "Regulations and Courses" from the Registrar, University of London, South Kensington, S.W.

Several valuable Scholarships and Exhibitions are available to students.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry—W. H. Perkin, M.A., F.R.S.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years. Students of Chemistry can obtain the degree of B.A. by passing preliminary examinations in Arts and in Science, and a final Honour examination in Chemistry. Chemistry may also be taken as part of the examination for a Pass degree. Graduates of other Universities and other persons suitably qualified can obtain the degree of Bachelor of Science after an approved course of study or research and two years' residence.

University Laboratory.—Demonstrators, J. E. Marsh, M.A., F.R.S., N. V. Sidgwick, M.A., A. F. Walden, M.A., B. Lambert, M.A., F. D. Chattaway, M.A., F.R.S.—The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

Large new Laboratories have been erected which, it is hoped, will be ready for occupation in October.

There are also laboratories which specialise in different parts of the subject:—*Physical Chemistry*, Balliol and Trinity College Laboratory: D. H. Nagel, M.A., H. B. Hartley, M.A. *Inorganic Chemistry*, Christ Church Laboratory: A. Angel, M.A. *Quantitative Analysis*, Magdalen College Laboratory: J. J. Manly, M.A. *Jesus College Laboratory*: D. L. Chapman, M.A. F.R.S. *Queen's College Laboratory*: Rev. G. B. Cronshaw, M.A.

Scholarships of about the value of £80 are obtainable at the majority of the colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the Examination Statutes; the Student's Handbook to the University; and from the professors and college tutors.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry—William J. Pope, M.A., F.R.S. *Jacksonian Professor of Natural and Experimental Philosophy*—Sir James Dewar, M.A., F.R.S.

Goldsmiths Reader in Metallurgy—Charles T. Heycock, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in any term of residence or before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

A graduate of another University may be admitted as a Student of Research, and obtain a degree after two years' residence in the University, by presentation of a thesis describing original research.

Facilities for research work are provided both in the Chemical Laboratories and in the Metallurgical Laboratories.

The scholarships, ranging in value from £20 to £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science at the several Colleges; the dates of the examinations vary, but are always fully advertised.

The Chemical Laboratories of the University are open daily for the use of the Students. The Demonstrators attend daily to give instruction. A list of the lectures and practical courses is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registry, Cambridge, from the *Cambridge University Calendar*, or from the "Students' Handbook to Cambridge."

UNIVERSITY OF DUBLIN.

TRINITY COLLEGE.

Professor of Chemistry—Sydney Young, D.Sc., F.R.S. *Professor of Applied Chemistry*—Emil A. Werner, Sc.D., F.C.S., F.I.C.

Demonstrator—W. C. Ramsden, F.C.S.

Junior Demonstrator—H. Krall, B.A., B.Sc.

The general Quantitative and Research Laboratories include working accommodation for about 130 Students. The Laboratories will open on October 1st. Lectures will commence on November 4th.

The Laboratories and the Lectures of the Professor of Chemistry can be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The Lectures delivered are:—

1. *Inorganic Chemistry and Chemical Philosophy*.—Elementary, first year; Advanced Inorganic Chemistry, second year; Physical Chemistry, third year.
2. *Organic Chemistry*.—General, second year; advanced, third year.
3. *Metallurgy*.—A Course for Engineering and Technical Students.
4. *Agricultural Chemistry*.—Theoretical and Practical Courses.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The *Summer Course of Practical Chemistry for Medical Students* begins early in April and terminates about the middle of June.

A special course for Dental Students will be given.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

By recent decrees, Prizes in Chemistry and Physics will be given in future at the October (Arts) Entrance Examination, and also at the Terminal Examinations of the Junior and Senior Freshmen Years.

Similarly, two Science Scholarships will be obtainable by Undergraduates, and tenable for five years. The Foundation Scholars receive £20 per annum, they have free commons, and their chambers for half the charge paid by other students; their tutorial fees are at one-fourth the usual rates.

KING'S COLLEGE.

(UNIVERSITY OF LONDON).

Professors—Herbert Jackson, F.C.S., &c. (Daniel Professor), and A. W. Crossley, Ph.D., F.R.S., &c.
Assistant Professor—P. H. Kirkaldy, F.C.S., &c.

Lecturers and Demonstrators—S. W. Collins, B.Sc., L. E. Hinkel, B.Sc., H. W. Cremer, B.Sc., and H. G. T. Boorman, B.Sc.

The Academical Year consists of Three terms. The days fixed for the commencement of Terms in 1915-1916 are Oct. 6, Jan. 12, and May 3.

The general Courses of Lectures on Chemistry deal with the nature and scope of the subject and the principles involved, in relating to one another the experimental facts, shown as illustrations of the properties of the elements and their chief compounds. The non-metallic elements are first treated of, as demonstrating most clearly the characters of the interactions between the different kinds of matter, and as affording the best opportunity of classifying the main groups of compounds met with, when dealing with the inorganic branch of the subject. The metallic elements and their compounds are then discussed, and this part of the Course is completed with a *résumé* in which the connected relations of the properties of the elements are described. The latter portion of the Course embraces in the same manner a study of the principles and properties of the carbon compounds which are examples of the main groups of organic substances. Class Examinations are held from time to time during the Session.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till five daily, except Saturday.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

For fuller details the separate Syllabuses provided for each class should be consulted.

UNIVERSITY COLLEGE.

(UNIVERSITY OF LONDON).

Professors—J. Norman Collie, Ph.D., F.R.S. (Organic Chemistry); F. G. Donnan, M.A., F.R.S. (Inorganic and Physical Chemistry).

Assistants—S. Smiles, D.Sc.; Katharine A. Burke, B.Sc.; R. E. Slade, D.Sc.; W. B. Tuck, D.Sc.; Irvine Masson, M.Sc.; H. Terrey, B.Sc.

The Session is divided into three Terms, as follows:—

First Term, from October 4 to December 22; Second Term, from January 13 to March 29; Third Term, from May 2 to July 6.

Introductory Course of Inorganic Chemistry.

Tuesday and Thursday, at 11. Practical, Thursday, 2 to 3.30, or 3.30 to 5. Fee, £10 10s.

The principles of Elementary Inorganic Chemistry, illustrated chiefly by reference to:—Air, water, salt, ores, fuels, coal industry, furnace products, soda industry, mortar, cement, glass making, nitre and nitrogen-fixation; other technical processes, and the properties of metals.

Junior Course of Inorganic Chemistry.

An Introduction to the Principles of Inorganic Chemistry. Special attention will be paid to general points of view, and to the application of physico-chemical laws and methods.

First and Second Terms: The Class meets three times a week, on Mondays, Wednesdays, and Fridays, at 9, for Lectures, Examinations, and Exercises.

Third Term: Lectures will be given on Mondays, Fridays, and Saturdays at 9, and Wednesdays at 11.

Fees: Course, £7 7s.; First or Second Terms, £4 4s.

A Practical Class will meet throughout the Session.

Senior Course of Physical Chemistry.

Tuesday and Thursday at 9.

A general Course on Physical Chemistry and its applications.

Fee:—Course, £5 5s.

General Course of Organic Chemistry.

Monday and Wednesday at 12, Thursday at 3.

Fees:—For the Course, £6 6s.; for a Term, £2 12s. 6d.

An Advanced Course will be held twice a week throughout the Session for those engaged in prosecuting research in Organic Chemistry. Monday and Friday at 11. Fee, £5 5s.; Term, £2 2s.

Practical Classes.

Practical Classes in Inorganic and Organic Chemistry are conducted by the Assistants.

Laboratories of General and of Organic Chemistry.

The Laboratories are open daily from 9 a.m. to 5 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

When accompanied by, or preceded by, attendance on the Lectures and Practical Classes in Inorganic and Organic Chemistry, the Laboratory Courses qualify Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. Several valuable Scholarships are available to students.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY.

Emeritus Professors—Sir W. A. Tilden, D.Sc., F.R.S., and Sir T. E. Thorpe, C.B., F.R.S., &c.

Professor and Director of the Chemical Laboratories.—H. Brereton Baker, D.Sc., F.R.S., &c.

Professor of Chemical Technology and Fuel Chemistry.—W. A. Bune, F.R.S.

Professor of Organic Chemistry.—J. F. Thorpe, F.R.S.

Professor of Physical Chemistry.—J. C. Philip, M.A., D.Sc.

Assistant Professor.—B. Mouat Jones, M.A.

The Imperial College of Science and Technology, incorporated under the Royal Charter of July 8, 1907, is an institution or group of associated colleges with its principal seat at South Kensington,

The purposes of the Imperial College are to give the highest specialised instruction, and to provide the fullest equipment for the most advanced training and research in various branches of science, especially in its application to industry; and to do all and any of such things as the Governing Body consider conducive or incidental thereto, having regard to the provision for those purposes which already exists elsewhere.

For these purposes, the Governing Body, subject to the provisions of the Charter, are to carry on the work of the Royal College of Science, and the Royal School of Mines, and may establish Colleges and other Institutions or Departments of Instruction. Any Institution or Department so established, and, subject to the conditions of the Charter, the Central Technical College of the City and Guilds of London Institute, are to be integral parts of the Imperial College; and the Central Technical College is to be called and known in future as the City and Guilds College.

The Charter further provides that the Imperial College shall be established in the first instance as a School of the University of London. Students of the Imperial College who have matriculated at the University of London may therefore proceed to the Science degree of the University as "Internal Students."

Attention is particularly directed to the conditions of admission and to the extended facilities for Research Work.

The ordinary courses of instruction are planned so as to extend over four years, and are generally similar for all divisions during the first year, and to a less extent during the second year, after which they are specialised according to the particular course which the student is taking.

The following Diplomas are awarded to Students of the several constituent Colleges:—

The Diploma of the Imperial College of Science and Technology (D.I.C.) for advanced study or research in Pure or Applied Science.

The Associateship of the Royal College of Science (A.R.C.S.) in one or more of the following divisions:—Mechanics, Physics, Chemistry, Botany, Zoology, Geology.

The Associateship of the Royal School of Mines (A.R.S.M.) in one or more of the following divisions:—Metallurgy, Mining.

The Associateship of the City and Guilds Institute, (A.C.G.I.) in Engineering (Civil and Mechanical), Engineering (Electrical).

Twelve entrance scholarships are given in September each year, and post graduate scholarships are available for enabling fourth and fifth year students to complete their course. Three Research Fellowships, founded by Mr. Otto Beit, of £150 a year, tenable at the Imperial College, are offered annually to post graduate students of this College, as well as to graduates of other Universities.

Full details can be obtained from the College Calendar published by Eyre and Spottiswoode (or through any bookseller), price 6d.

THE SCHOOL OF PHARMACY OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

Professors—Chemistry, Henry L. Smith, B.Sc., F.I.C.; Pharmaceutics, Henry G. Greenish, F.I.C., F.L.S. (Dean).

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry, Botany, Materia Medica, and Pharmacy commences in October and terminates at the end of June. An Advanced Course of Lectures begins in October and extends to the end of March. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also of those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. Certificates of attendance at the Lectures and Practical Work in Chemistry and in Botany are accepted as evidence of

scientific training by the Institute of Chemistry in connection with the Examinations for the Associateship. Certificates of attendance at the Lectures and Practical Work in Chemistry are accepted by the Conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies. Certificates of attendance at the Course of Pharmacy are also accepted by the Conjoint Board, and at the Courses of Pharmacy and Materia Medica by the University of London for the Second Examination for Medical Degrees, Part II.

Prospectuses and further information may be obtained from the Dean of the School, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

UNIVERSITY OF WALES.

Professor—A. Findlay, M.A., D.Sc. (Aberdeen), Ph.D. (Leipzig), F.I.C.

Lecturer and Demonstrator—T. Campbell James, M.A., Trinity College, Cambridge, D.Sc. (Wales).

Assistant Lecturer and Demonstrator—Vacant.

Lecture Assistant—Vacant.

Student Assistant—Vacant.

Lecturer in Agricultural Chemistry—J. Jones Griffith, B.Sc. (Wales).

The College is open to men and women students above the age of sixteen years. The Session commences on Oct. 5th, on which day all Students will be expected to meet the Professors in the Examination Hall of the College.

Lecture Courses.—(1) Intermediate Science Course; four lectures weekly throughout the Session. (2 and 3) B.Sc. Courses; A, three lectures weekly on Organic Chemistry; B, three lectures weekly on General and Physical Chemistry. (Courses A and B will generally be given in alternate Sessions; for 1915-1916, Course A). (4 and 5) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly during the Michaelmas and Lent terms.

Laboratory Courses.—The Laboratories are open daily from 9 a.m. to 1 p.m. and from 2 to 6 p.m., Saturdays 9 a.m. to 1 p.m. Regular Courses of practical work, suitable for the B.Sc. degree of the Universities of London and Wales, or for the Associateship of the Institute of Chemistry, can be followed. Facilities are given for Students wishing to undertake research work. Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the University of Edinburgh and the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland, and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spent at Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £17. This composition fee enables the Student to attend any or all the Classes and Laboratories of the College.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 21, and exhibitions are awarded at the end of the Session on the results of the class examinations.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Prospectuses issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES,
BANGOR.

A CONSTITUENT COLLEGE OF THE UNIVERSITY OF WALES.

Chemistry.—Professor, K. J. P. Orton, M.A., Ph.D., F.I.C. Assistant Lecturers and Demonstrators, J. O. Hughes, B.Sc., Sybil M. Leslie, M.Sc., Lecturer in Agricultural Chemistry, H. E. Jones, B.A., B.Sc.

Physics.—Professor, E. Taylor Jones, D.Sc. Assistant Lecturers and Demonstrators, A. H. Ferguson, D.Sc., and W. E. Williams, B.Sc.

The Session opens October 5th, 1915. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Session, £5.

B.Sc. Course.—Organic Chemistry. Fee for the Session, £3 15s. Advanced Lectures on Organic Chemistry, £1 5s. Physical Chemistry, £1 5s.

Agricultural Chemistry.—Fee, £2 10s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 5 p.m. for instruction in Chemical operations and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; Composition Fee for all Lectures and Laboratory Classes of the Science Degree Course taken in one year, £16.

The College Courses are arranged with reference to the Degree Courses of the University of Wales (of which the College is one of the Constituent Colleges). The Courses in Science are also suited to the requirements of Students preparing for the Science Degree Course of the University of London.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and by the Conjoint Boards of the Royal Colleges of Surgeons and Physicians, and students can make one *Annus medicus* at the college. Students are prepared for the First Examination of the Universities mentioned, the First Examination for Medical Degrees of the University of London, and of the Conjoint Board of the Royal Colleges of Surgeons and Physicians. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES
AND MONMOUTHSHIRE, CARDIFF.

Professor of Chemistry—C. M. Thompson, M.A., D.Sc., F.C.S.

Assistant Professor—E. P. Perman, D.Sc., F.C.S.

Lecturer to Medical Students and Demonstrator—R. D. Abell, D.Sc., Ph.D., F.I.C., F.C.S.

Professor of Metallurgy—A. A. Read, D.Met., F.I.C., F.C.S.

Assistant Lecturer and Demonstrator—R. H. Greaves, M.Sc.

The Session commences October 5th and terminates on June 23rd, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 30 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London. Fee, £2 10s.

The Intermediate Course consists of about 80 lectures; together with laboratory practice it forms the qualifying course for the Intermediate Examination of the University of Wales, and will cover the subjects required for the Intermediate Examination in Science (Part I.) of the University of London. Fee, £4 10s.

The Senior Course consists of about 80 lectures on Organic Chemistry; Fee, £3 15s.

A course on Inorganic Chemistry will be given in the Session 1915–1916.

In the laboratory each student works independently, so that the course of study may be adapted to the require-

ments of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £4 per session; eight per week, £6 6s. per session; twelve hours or more per week, £8 8s. per session.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

Students by making a payment of £16 at the commencement of each session may compound for all fees for the whole session.

At the entrance examination in April, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A special prospectus is issued concerning courses of study for diplomas in engineering, mining, and metallurgy.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY OF BRISTOL.

DEPARTMENT OF CHEMISTRY.

Alfred Capper Pass Professor of Chemistry—Francis Francis, D.Sc., Ph.D., F.I.C.

Lecturers—O. C. M. Davis, B.Sc., D.Sc., F.I.C.; F. W. Rixon, M.Sc., Ph.D.

Lecturer in Physical Chemistry—James W. McBain, M.A., Ph.D.

Lecturer in Bio-chemistry—Max. Nierenstein, Ph.D.

Lecturer in Hygienic Chemistry—Edward Russell, B.Sc., F.I.C.

Lecture Assistant—J. H. Sturgess.

The session commences on October 1.

The Department of Chemistry is situated in the new wing of the University Buildings in Tyndall's Park, and was opened on October 1, 1910. The Department provides accommodation for 200 students, and laboratories for work in specialised branches of Chemistry have been designed and equipped with apparatus of the most modern type. All the laboratories are supplied with electric wiring for experimental purposes, and currents of any desired voltage up to 250 volts at 50 amperes from dynamo or storage cells may be obtained throughout the Department. Higher voltages and currents are available in special laboratories, for Physical Chemistry and Electro-metallurgy. Special facilities are afforded to those who desire to carry out research or to study Chemistry as applied to the different processes employed in the arts and manufactures; and a laboratory for Bio-chemistry has been specially designed for the investigations of problems on Biological lines.

DAY LECTURES.

General Courses.—1. General Inorganic Chemistry—Three lectures per week during Session and Laboratory work. 2. General Organic Chemistry—Three Lectures per week during one Session and Laboratory work. 3. Physical Chemistry—Three Lectures per week for first Session, two Lectures per week for second Session, and Laboratory work.

The Laboratories are open daily from 9.30 to 5 except on Saturdays, when they are open for Senior Students only.

Courses for Graduation.—*Intermediate Science*—Course 1 and one day Laboratory per week. *Pass Degree*—Course 2 and 3, and at least one day Laboratory per week during two Sessions. The Chemical Society must be attended during the second and third years, and one or more of the Special Courses arranged for Honours Students. *Honours Degree*—Three year course after

passing the Intermediate Examination (which may be taken on entering the University). The last session is spent on research which is essential for all Honours Degrees in the Faculty of Science. During the first year in the Honours School Courses 2 and 3, and the second and third, Course 3, and one or more of the following Special Courses as directed, e.g.—Organic Chemistry, Physical Chemistry, Mathematical Chemistry, Advanced Inorganic Chemistry, Applied Electro-chemistry, some part of Bio-chemistry.

The meetings of the Chemical Society must be attended during each Session.

Colloquium.—A weekly Colloquium will be held by members of the Staff to discuss recent advances in the various developments of Chemistry. Honours Students attend, and others interested are invited to do so.

Extract from Regulations as Regards Fees.

1. Registration Fee 7s. for a single Course; £1 1s. shall cover a perpetual registration for any number of Courses.
2. Inclusive Fee for an entire curriculum for degree of B.Sc., whether "Pass" or "Honours," shall be £21 a year.
3. The Fees for separate Courses of Lecturers in Faculty of Science shall be at the rate of £1 1s. per term, or £2 2s. a year for each hour per week for which the Course in question is offered.

The Fees for separate Laboratory practice and instruction in the Faculty of Science shall be at the rate of £2 2s. per term for each day in the week for which admission in the Laboratories is sought, with a minimum of £3 3s. in each particular case.

EVENING LECTURES.

The Laboratories are opened, for students who have attained the standard of an Inter. B.Sc. examination, from 6.30 to 9.30 p.m. on Tuesday during the Autumn and Spring Terms. Course 1 will be given on Wednesday at 8 to 9, and Course 2 or 3 on Friday at 8 to 9 p.m. during these Terms. The Lectures and Laboratory work in Course 1 will be similar to that given to Second year Students in the Faculty of Science, and that given in Course 2 or 3 to one of those given to Students studying or the Final Degrees in that Faculty.

Extract from Regulations as Regards Fees for Evening Students.

1. For Evening Students who enter on a curriculum for a Degree the Registration Fee shall be 5s., for a curriculum for a Certificate, unless the Student has matriculated, the fee shall be 10s. 6d.
2. Unless in any case otherwise prescribed, the Fees for Evening Classes in the Faculties of Arts and Science shall be 10s. 6d. for two terms, or for one term's attendance.

All communications to the University to be addressed to the Registrar. Information concerning Courses or Laboratory work in the Department of Chemistry may be obtained from the Professor.

The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratories. The Department of Engineering is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, mining, or motor car engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the University into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the University. Several Scholarships are tenable at the University.

MERCHANT VENTURERS' TECHNICAL COLLEGE, BRISTOL.

CHEMISTRY.

Professor—J. Wertheimer, B.A., D.Sc., F.I.C., F.C.S.
Lecturers—H. A. M. Borland, A.R.C.S.; Annie M. Herbert, B.Sc.

Demonstrators—E. G. Moody and W. J. Gibbs.

Assistant in Chemical Laboratory—A. Withy.

In consequence of the foundation of the University of Bristol, the College now restricts its work to Applied Chemistry in the daytime; Pure Chemistry is taught in the Faculty of Science of the University of Bristol. The Engineering work of the late University College has, on the other hand, been transferred to this College.

The College Evening Classes commence on Monday, Sept. 20th.

Further detailed information may be obtained from the College Calendar, price 61., or the Prospectus for Day or Evening Classes (1d. each).

UNIVERSITY OF BIRMINGHAM.

Professor—Percy F. Frankland, Ph.D., Sc.D., LL.D., F.R.S., F.I.C.

Assistant Lecturers and Demonstrators—Hamilton McCombie, M.A., Ph.D., B.Sc., A.R.C.S., A.I.C.; S. R. Carter, M.Sc.; A. Parker, M.Sc.; J. E. Coates, M.Sc.

Professor of Metallurgy—Thomas Turner, M.Sc., A.R.S.M.

The Session will be opened on October 5th, 1915.

The Chemical Department has hitherto been housed in the new University buildings at Bournbrook, but owing to those buildings having been taken over by the Military Authorities for use as a Base Hospital the classes during the coming Session will be arranged for at the Birmingham Municipal Technical School and the Mason College.

Lecture Courses.

First Year.—A. This part of the course is arranged (1) to give a full exposition of the general principles of Chemical Science, (2) for the systematic study of the properties of the more important elements and their compounds, and (3) to indicate the chief applications of Chemistry in the Arts and Manufactures. Three hours weekly during the Winter and Spring terms. Mondays, Wednesdays, and Thursdays at 9.30 a.m. Fee, £4 4s. B. This part of the course includes an introduction to the study of Organic Chemistry, with a description of the properties, relations, and methods of preparation of the more important groups of Carbon Compounds. Three hours weekly during the Summer term. Mondays, Wednesdays, and Fridays, at 9.30 to 10.30 a.m. Fee, £1 11s. 6d.

Second Year.—*Advanced Organic Chemistry.*—This course extends over two years, and is divided into two parts:—(a) Carbon Compounds of the Fatty Series; (b) Aromatic and other Cyclic Compounds. Only one of these parts will be taken in each year. The class meets twice weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. *Advanced Inorganic Chemistry.*—This course is devoted to the consideration of special branches of Inorganic Chemistry, and direction is also given as to the private reading which should be pursued by students. The class meets by arrangement once weekly during the Session. Fee, £1 1s.

Third Year.—A further Course in Advanced Organic Chemistry will deal with one of the above parts of the Course. The class meets two hours weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. A Course on Physical Chemistry. Fee, £2 2s.

The class meets two hours weekly during the Winter and Spring Terms.

Fourth Year.—For students preparing for the B.Sc. degree with Honours in Chemistry.

Special Courses in General, Organic, and Physical Chemistry.

Practical Chemistry.

The instruction in Practical Chemistry (Inorganic, Organic, and Physical) extends over four years in the

case of the Honours Degree. The Laboratory will be open daily from 9.30 to 5, except Saturdays, when it closes at 1 p.m. Fees—

	All day.	Three hours per day.	Three hours per day; five days a week.	Three hours per day; three days a week.
	Guineas.	Guineas.	Guineas.	Guineas.
One Term ..	7	4½	4	2½
Two Terms ..	13	8½	7½	5
Three Terms	18	12	11	6½

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee. Special facilities are given to Advanced Students for the prosecution of original research.

Metallurgy.

There is a separate University department for Metallurgical students in which provision is made for instruction in assaying, &c.

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of about £96 each are awarded annually in June.

Ascough Scholarship.—One Open Scholarship of the value of about £30 is awarded annually in July.

Bowen Scholarship.—One Open Scholarship in Metallurgy, value about £96, is awarded annually in June.

For particulars apply to the Registrar.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturers.

CITY OF BRADFORD TECHNICAL COLLEGE.

Principal—Prof. W. M. GARDNER, M.Sc., F.I.C.

DEPARTMENT OF CHEMISTRY AND DYEING.

Professor of Chemistry and Dyeing—The Principal.

Assistant Professor of Chemistry—B. North, A.R.C.S. (Lond.).

Lecturers in Chemistry—L. L. Lloyd, Ph.D.; H. Middleton, M.Sc.; N. Bland, M.Sc.; A. Jackson, B.Sc.

Lecturer in Physics—J. A. Tonkins, A.R.C.S. (Lond.).

Demonstrator in Physics—F. Harcourt, B.Sc.

Lecturer in Dyeing—M. Fort, M.Sc.

Lecturer in Gas Manufacture—J. W. Roper.

Lecturer in Botany—J. Cryer.

Lecturer in Pharmacy—G. H. Etchells.

Lecturer in Biology—J. A. Fisher.

The following courses of instruction are provided—

I. *General Chemistry Course*, extending over four years, and including Lectures in Inorganic, Organic, and Technological Chemistry, Principles of Analysis, Technical Analysis, Electro-chemistry, Physical Chemistry, Physics, Mathematics, Mechanics, with Laboratory work in Chemistry and Physics.

II. *Chemistry and Dyeing Course*, extending over four years. Includes most of the above subjects, along with Lectures and practical work in Dyeing, Colour matching, &c. The practical laboratories include a completely equipped Practical Dyehouse and Finishing Rooms.

III. *Chemical Engineering*. Three years' course, preparing Students for positions in Chemical Works, Sewage Works, &c.

IV. *Sanitary Science*. One year's Course, recognised by the Sanitary Institute as preparing for their certificate examination. Subjects: Chemistry, Physics, Sanitary Engineering, Sanitary Law, Building Construction, Drawing, Physiology, and Bacteriology.

V. *Dyeing*. Special Courses for Graduates in Chemistry, and for Drysalter, Colour Merchants, &c.

VI. *Textile and Dyeing*. Arranged for those Students who desire to study the two subjects simultaneously.

VII. *First Professional Examination, Conjoint Medical Board (M.R.C.S., L.R.C.P.)*, London.—Attendance at the College and College Certificates in Chemistry, Physics, and Biology are recognised by the Conjoint Boards for Medical Studies (London and Dublin) as a qualifying curriculum.

VIII. *General Pharmaceutical Course*. Prepares for the Minor, Major, and Assistants' Pharmaceutical Examinations. Each extends over two years on four half-days per week, and includes Chemistry and Physics, Botany, Biology, Materia Medica, Pharmacy, and Dispensing.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

CHEMICAL DEPARTMENT.

Professor—Prof. E. Kinch, F.C.S., F.I.C.

Demonstrator—(Killed in War).

Assistant—H. Douglas Elkington, B.Sc., F.I.C.

(Closed during the period of the war).

THE UNIVERSITY OF LEEDS.

Professor of Chemistry—Arthur Smithells, B.Sc., F.R.S.

Professor of Organic Chemistry—Julius B. Cohen, Ph.D., B.Sc., F.R.S.

Lecturer on Physical Chemistry—H. M. Dawson, D.Sc., Ph.D.

Assistant Lecturers and Demonstrators—W. Lowson, B.Sc., F.I.C.; W. H. Perkins, M.Sc., F.I.C.

Demonstrators—H. Calam, M.Sc., F.I.C.; J. Marshall, M.Sc.

Lecture Courses.

1. *General Course of Chemistry*.—Monday, Wednesday, and Friday, at 11.30 a.m. Fee for the Course, £5 10s.

2. *Advanced Inorganic Chemistry*.—(A) Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £4 10s.

3. *Advanced Inorganic Chemistry*.—(B) Tuesday, Thursday, and Saturday, at 9.30 a.m. Fee, £4 10s.

4. *Organic Chemistry*.—Tuesday, Thursday, and Saturday at 11.30 a.m. Fee £4 10s.

5. *Honours Courses*—(a) Organic Chemistry: Monday, Wednesday, and Friday at 11.30 a.m.; fee, £4 10s. (b) History of Chemistry: Monday, Wednesday, and Friday at 9.30 a.m. in the First Term; fee, £2 5s. (c) Physical Chemistry: Monday, Wednesday, and Friday at 9.30 a.m. in the Second and Third Terms; fee, £3 7s. 6d. (d) Electro-chemistry: Tuesdays at 9.30 a.m.; £2 10s.

6. *Chemistry of Food and Drugs*.—Special class during the second term for Students taking Final Examination of the Institute of Chemistry in Branch E (Food and Drugs). £3 3s. *Laboratory Courses.*

The University Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session—£3 per half day of three hours per week.

Practical Course in Sanitary Chemistry.—Tuesdays and Thursdays from 2 to 5 in the Second and Third Terms Fee, £7 7s.

Tinctorial Chemistry and Dyeing Department.

Professor—Arthur G. Green, M.Sc., F.I.C., F.R.S.

Lecturer and Research Chemist—A. G. Perkin, F.R.S., F.I.C.

Assistant Lecturer—G. H. Frank, M.Sc., F.I.C.

The Courses extend over periods of three or four years, and are intended for those who wish to obtain a full scientific and practical education in the art of dyeing, colour manufacture, &c. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, e.g., the sons of manufacturers, calico printers, managers, master dyers, &c., or in the manufacture of coal-tar products and dyestuffs.

Leather Industries Department.

Professor—H. R. Procter, D.Sc., F.I.C.

Assistant Lecturers and Demonstrators—Harold Brumwell; W. R. Atkin, M.Sc.

Demonstrator—F. C. Thompson, M.Sc.

The full Courses, which extend over a period of either two or three years, are suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and are recommended to sons of tanners. The Courses include instruction in chemistry, a modern language, leather manufacture, and practical work in the Leather Industries Laboratory and Dye-house.

Agricultural Department.

Professor—R. S. Seton, B.Sc.

Professor of Agricultural Chemistry—C. Crowther, M.A., Ph.D.

The full Course occupies three years, and includes instruction in chemistry, physics, mathematics, geology, botany, forestry, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out door agriculture at the University Farm.

Department of Coal-gas and Fuel Industries with Metallurgy.

Livestry Professor—J. W. Cobb, B.Sc., F.I.C.

Assistant Lecturer and Demonstrator—H. J. Hodsman, M.Sc.

Research Chemist—W. Harrison, M.Sc.

The Courses extend over two, three or four years, and are suitable for those who are preparing for posts either as Gas Engineers or in Fuel and Metallurgical industries.

The Courses in Gas Engineering and the Technology of Fuel will chiefly deal with the manufacture and distribution of coal-gas and gas-lighting problems, by-product coking processes, and the production and application of gaseous fuels for heating and power purposes.

The Metallurgical Courses, besides dealing with general processes for the concentration and extraction of ores, will be chiefly directed to problems underlying blast furnace and open-hearth steel practice, and to the micro-structure, physical properties, and heat treatment of steel and other industrial alloys.

Research Students are admitted to the University Laboratories on reduced terms.

Several valuable Fellowships and Scholarships are at the disposal of the University, including a Fellowship of £100 offered by the Institution of Gas Engineers, and the Salt, Akroyd, Brown, Baines, Emsley, Craven, and Cloth-workers' Scholarships, and one of the 1851 Exhibition Scholarships. The Leeds City Council's and the North, East, and West Ridings County Council's Scholarships are tenable at the University of Leeds.

UNIVERSITY OF LIVERPOOL.

Professor of Inorganic Chemistry—E. C. C. Baly, M.Sc., F.R.S.

Professor of Physical Chemistry—W. C. McC. Lewis, M.A., Ph.D.

Professor of Bio-chemistry—W. Ramsden, M.A., D.M.

Professor of Organic Chemistry—R. Robinson, D.Sc.

Lecturer on Metallurgy—Guy D. Bengough, D.Sc., M.A., A.R.S.M.

Lecturer on Analytical Chemistry—A. Rule, D.Sc., Ph.D.

Assistant Lecturers and Demonstrators—A. J. Allmand, D.Sc.; C. S. Garrett, B.Sc.; Francis W. Kay, M.Sc., Ph.D.; J. Smeath Thomas, M.Sc.

Lecture Assistant—H. H. Froyell.

The Session commences October 5th.

Entrance Scholarship Examination takes place early in May each year.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in the University of Liverpool; for Degrees in Medicine of Liverpool; for the

Pharmaceutical, Veterinary, Dental, and Public Health Diplomas; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry and other Examination Boards.

Lecture Courses.

A. General Introductory Course, including the principles of Organic and Physical Chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, including Practical class, £6.

Course A.—General Elementary Chemistry, £4.

Course B.—Inorganic Chemistry. Fee, £3.

Course C.—Inorganic Chemistry (Honours Course). Fee, £4.

Course D.—Organic Chemistry. Fee, £3.

Course E.—Organic (Honours). Fee, £4.

Course F.—Physical Chemistry. Fee, £3.

Course G.—Honours Physical Chemistry. Fee, £4.

Course H.—Applied Inorganic Chemistry, £2 10s.

Course J.—Metallurgy. Fee, £2 10s.

Course K.—Applied Organic Chemistry. Fee, £2 10s.

Course L.—Electro-chemistry. Fee, £2 10s.

Also Pass and Honours Courses in Bio-chemistry.

Research students carrying out research work pay a fee of £3 per annum.

The Inorganic and Organic Chemical Laboratories provide accommodation for every kind of work and research in inorganic and organic chemistry and in metallurgy. There is also a laboratory devoted to spectroscopic work and research.

The Muspratt Laboratories of Physical Chemistry and Electro-chemistry adjoin the main chemistry buildings, and, owing to their full equipment, offer every opportunity or all manner of work and research in these subjects.

The Bio-chemical Laboratory is also separately housed, and provides facilities for work and research.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study, for which a full curriculum is provided. Fees:—

Per Week	One Term, Three Months.	Three Terms One Session.
One day	£4	£7
Two days	5 10s.	10
Three days	7	13
Whole week	10 10s.	21

D.P.H. Course (see special syllabus).

Course for Dental Degree and Diploma (see special syllabus).

Technological Curriculum.

The curriculum extends over three or four years.

The Final Examination for the Associateship of the Institute of Chemistry may be taken after the third year. Those students who have taken the Ordinary Degree of B.Sc. may pass the M.Sc. Exam. in any subsequent year.

The Sir John Willox Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1915, on an Examination in subjects which are included in the first two and a half years of the above curriculum. Candidates should send in their names to the Registrar not later than November 15. The Sheridan Muspratt Chemical Scholarship, on similar lines, is open for competition. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

Evening Classes.

Classes on Metallurgy will be held during the winter. Prospectuses containing particulars may be obtained from the Registrar, University of Liverpool.

ARMSTRONG COLLEGE, NEWCASTLE-ON-TYNE.
(IN THE UNIVERSITY OF DURHAM).

Professor of Chemistry—P. Phillips Bedson, M.A., D.Sc., F.I.C., V.P.C.S., J.P.

Lecturers in Chemistry—F. C. Garrett, D.Sc., F.C.S., and J. A. Smythe, D.Sc., Ph.D., F.C.S.

Assistant Lecturers and Demonstrators—A. Forster, M.Sc., Ph.D., and J. B. Firth, M.Sc.

Lecturer in Agricultural Chemistry—S. Hoare Collins, M.Sc., F.I.C., F.C.S.

Assistant Lecturer in Agricultural Chemistry—A. A. Hall, M.Sc., Ph.D.

First Year Courses.—Division I.—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 6 h. Fee, £3 10s. for the Session.

Division II. Similar to Division I., but modified to meet requirements of Students for Degrees in Engineering and Mining. Mondays 12 to 1, Tuesdays and Thursdays 10 to 11. Fee, £3 10s. for Session.

Second and Third Year Courses.—These lectures are designed to form a part of the course of instruction in Chemistry, and to prepare students for the examinations in Chemistry for the degree of Bachelor of Science, Pass and Honours.

(a) *Inorganic Chemistry.*—Advanced Course, Tuesdays and Thursdays at 11 a.m. Fees, Lectures, £3 10s. per session, and £1 10s. per term.

(b) *Organic Chemistry.*—Aliphatic and Aromatic Compounds, Tuesdays and Thursdays at 10 a.m. Fees, Lectures, £3 10s. per session; £1 10s. per term.

(c) *Organic Chemistry.*—Advanced Course, Tuesdays and Thursdays at 12 noon for part of the session. Fees, Lectures, £3 10s. per session; £1 10s. per term.

(d) *History of Chemistry and Chemical Philosophy.*—Saturdays at 10 a.m. Fees, Lectures, £3 10s. per session; £1 10s. per term.

(e) *Physical Chemistry.*—Tuesdays and Thursdays at 12 noon for part of the session. Fees, Lectures, £3 10s. per session; £1 10s. per term.

(f) *Analytical Chemistry.*—Fridays at 9.15 a.m. Fee, £1.

(g) *The Rarer Elements and the Periodic Law.*—Times to be arranged. Fees, Lectures, £3 10s. per session; £1 10s. per term.

Students taking Chemistry for Pass Degree will attend in their second year the course *a* and *f*, and in their third year the courses *b* and *d*, in addition to the necessary Laboratory practice.

Students taking Chemistry for Honours Degree will attend in their second year the courses *a*, *b*, and *f*, and in their third year the courses *c*, *d*, *e*, and *g*, in addition to the necessary Laboratory practice.

A Lecture Course in Analytical Chemistry will be given on Fridays, at 9.15 a.m. Fee for the course, £1.

Metallurgy and Assaying.—Lecturer, Prof. Louis, M.A., D.Sc., F.I.C., F.G.S.; Demonstrator, H. Dean, M.Sc., A.R.C.M. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry Assaying, and in the preparation and analysis of Alloys, &c. Fees as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10s.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees.*—Students working six days per week £5 10s. per term, £15 per session; one day per week, £2 per term, £5 per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the degree of Bachelor in Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must have passed the University Matriculation Examination.

Matriculation Examination.—In order to enter on a course of study for a Degree a student must have previously satisfied the Examiners in the following subjects:—(1) English, (2) English History, (3) Mathematics, (4) three of the following subjects, of which one must be a language:—(a) Religious Knowledge, (b) Latin, (c) Greek, (d) Ancient History, (e) French, (f) German, (g) some other language to be approved, (h) Experimental Science or Physics or Chemistry, (i) Botany or Zoology, (j) Mechanics, (k) Extra Mathematics, (l) Geography.

(i.). Candidates for degrees in Arts, who do not offer Latin in their Matriculation Examination or in the equivalent accepted as exempting therefrom, will be required to pass in Latin at a subsequent examination before entering upon the Arts course.

(ii.). Candidates for degrees in Commerce, who do not offer a Modern Foreign Language in their Matriculation Examination, or in the equivalent as exempting therefrom, will be required to pass in a Modern Foreign Language at a subsequent examination before entering upon the Commerce course.

(iii.). Candidates for degrees in Engineering (Civil, Mechanical, and Electrical) and in Naval Architecture will be required to take the following subjects from the list:—(1) English; (2) English History; (3) one of four languages—Latin, Greek, French, German; (4) Experimental Science; (5) Extra Mathematics; (6) Geography.

(iv.). Foreign Students may be exempted from the Matriculation Examination on report from the Board of Professors of Armstrong College, that they have received such an education in their own country as will enable them to profit by University study, and that they have sufficient knowledge of English to enable them to follow the courses of instruction they are entering for.

For detailed Syllabuses and complete Regulations the College Calendar should be consulted.

Bachelorship in Science.—The degree of Bachelor of Science is conferred in Pass and Honours in Pure and Applied Science. For details of curricula, &c., the College Calendar should be consulted.

Exhibitions.—Two Exhibitions of the value of £20 and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Thursday, Sept. 30th, 1915. Candidates should send in their names to the Secretary on or before September 10th.

Several valuable Scholarships are available for students, including the Johnston Chemical Scholarship of the value of £60 for one year, which is open to Bachelors of Science of any British University; the examination for this Scholarship will be held during the week commencing October 4th. Candidates should send in their names to the Secretary on or before September 27th.

THE UNIVERSITY OF MANCHESTER.

Professor of Chemistry and Director of the Chemical Laboratories—Harold B. Dixon, M.A., M.Sc., Ph.D., F.R.S.

Professor of Organic Chemistry—Arthur Lapworth, D.Sc., F.R.S.

Reader in Biochemistry and Senior Lecturer in Chemistry—C. Weizmann, Ph.D., D.Sc.

Senior Lecturers and Demonstrators—Norman Smith, D.Sc.; E. C. Edgar, D.Sc.; and F. P. Burt, D.Sc.

Assistant Lecturers and Demonstrators—Edward Hope, D.Sc.; J. E. Myers, M.Sc.; W. J. Jones, M.Sc.; J. R. Partington, M.Sc.; and Colin Campbell, M.Sc.

Professor of Metallurgy—C. A. Edwards, D.Sc.

Assistant Lecturer in Metallurgy—W. E. Thornycroft, B.Sc., M.Sc.

Lecturers in Electro-Chemistry—J. N. Pring, D.Sc.; E. Newbury, D.Sc.

The Session begins October 7th, 1915.

Chemistry Lecture Courses.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

This course is intended for Students commencing the study of chemistry.

Introduction to Organic Chemistry.—Mondays, Wednesdays, and Fridays, at 11.30, during the Summer Term.

This course is designed to meet the requirements of Students preparing for the Intermediate B.Sc. Examination.

Biochemistry, Theoretical and Practical.—Tuesdays and Thursdays during the Summer Term. This Course prepares for Part III. of the first M.B. Examination.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30, during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Mondays, Wednesdays, and Fridays, at 2, during the two Winter Terms. The Metals.

Third Year Honours Course.—Theoretical and Physical Chemistry.

Organic Chemistry (General).—Mondays, Wednesdays, and Fridays, at 9.30, during the two Winter Terms.

Organic Chemistry (Advanced).—Tuesdays and Thursdays, at 9.30, during the two Winter Terms.

History of Chemistry.—Short Courses during the two Winter Terms.

Chemistry of Colouring Matters.—Theoretical and Practical Course during the Winter Terms.

Metallurgy.—Introductory Course, followed by either—(A) Lead, Copper, Bismuth, Antimony, Zinc, and Tin; or (B) Iron and Steel. Course A, two Lectures per week during the first half of the Session. Course B, one Lecture per week during the Session.

Electro-chemistry.—General Theoretical Course: One hour per week during the Michaelmas and Lent Terms. Applied Course: One hour per week during Michaelmas and Summer Terms.

B.Sc. with Honours in Chemistry.—The course extends over three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

The Research Laboratories for Inorganic, Organic, and Physical Chemistry, and for Metallurgy, are open to graduates and other advanced students.

For further particulars of any of these courses apply to the Registrar, Edward Fiddes, M.A., or to the Director of the Laboratories.

UNIVERSITY COLLEGE, NOTTINGHAM.

DEPARTMENTS OF CHEMISTRY AND METALLURGY.

Professor of Chemistry—F. Stanley Kipping, Ph.D., D.Sc., F.I.C., F.R.S.

Demonstrators of Chemistry—R. M. Caven, D.Sc., F.I.C.; E. B. R. Prideaux, M.A., D.Sc.; and H. Lambourne, B.Sc.

The Classes of the College are open to students of both sexes above sixteen years of age.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student attends a course on Inorganic Chemistry. In his second year he attends Lectures on both Inorganic and Organic Chemistry. In his third year he attends courses on Advanced

Organic Chemistry, Physical Chemistry, and Advanced Inorganic Chemistry.

Demonstrations and Lectures on Analytical Chemistry are given, and Chemical Calculation and Tutorial classes are also held. Various short courses of lectures on special subjects are delivered during the Session.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry and Metallurgy.—The Chemical and Metallurgical laboratories are open every day from 9 to 5, except on Saturday, when the hours are from 9 to 1; also on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Metallurgy, Dyeing, Brewing, Iron and Steel, and other Manufacturing Processes.

Research Work.—Students or others wishing to undertake research work in pure or Applied Chemistry will be afforded every facility for doing so and may be admitted at reduced fees. The Laboratories are fully equipped with apparatus and chemicals necessary for such work.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Gas Manufacture, and on other processes of applied Chemistry.

Pharmaceutical Students are provided with Lectures and Laboratory work suitable for the preparation for the Minor and Major Examinations.

The composition fee for full time in the Chemistry Department (lectures and laboratory) is £6 per term, and this fee covers all necessary apparatus and chemicals.

A composition fee of £6 per term is also charged for various complete courses, such as those required for the Institute of Chemistry, and for the degree examinations of London University.

Evening Classes.—Evening Lectures and Laboratory instruction will be given in Pure and Applied Chemistry, and the laboratories are open for practical work on Tuesday and Thursday evenings from 7 to 9. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

Full information concerning all College Classes is given in the College Prospectus, free from the Registrar.

THE UNIVERSITY OF SHEFFIELD.

Professor of Chemistry—W. P. Wynne, D.Sc., F.R.S.

Lecturers and Demonstrators—W. E. S. Turner, D.Sc., M.Sc.; W. J. Jarrard, B.Sc.; J. Kenner, D.Sc., Ph.D.; C. R. Young, D.Sc., B.Sc.

The Session will commence October 6th.

Matriculation Course.—Tuesday and Friday at 9.30, Wednesday at 11.30 during Michaelmas and Lent terms. Fee, £2 12s. 6d., and three hours per week Laboratory work.

Candidates for the Intermediate Examination are required to satisfy the Examiners in three of the following subjects:—Pure Mathematics, Applied Mathematics, Physics, Chemistry, Zoology, and Botany. And those for the Final Examination in three of the following subjects:—Pure Mathematics, Applied Mathematics, Physics, Chemistry, Zoology, Botany, Physiology, Geology, Education, Geography.

Intermediate Course in Chemistry for B.Sc. or M.B., Ch.B. or B.Met.—Monday, Wednesday, Thursday, and Saturday at 9.30 a.m. £5 5s., and six hours per week Laboratory work during first year.

B.Sc. Course in Chemistry.—Monday at 9.30 a.m. and Friday at 12.30 p.m. during second year, £3 3s.; Wednesday at 12.30 p.m., during two terms, Monday at 12.30 p.m. and Thursday at 11.30 a.m., during third year, £3 3s.; and nine hours per week Laboratory work during second and third years.

B.Sc. with Honours.—Honours Students in Chemistry, after passing the Intermediate Examination, devote the whole of their time to the study of Chemistry, and are expected to reach the standard for a pass in Chemistry for the ordinary degree by the end of the second year. During the second or third year they devote one day a week to lectures and practical work in a subsidiary subject—Mathematics, Physics, or Metallurgy—selected for the degree. The third year is devoted to the advanced study of Chemistry, either chiefly Physical and Inorganic or chiefly Organic, as the student may select. At least four days a week during the second and third years are spent in the laboratory.

M.Sc.—This degree may be conferred upon a Bachelor of Science with Honours who is of one year's standing from the date of his graduation as a Bachelor of Science, or upon a Bachelor of Science who has either passed an examination in an Honours School subsequent to graduation, or has for at least one year after graduation done research work at the University, and has presented a thesis, approved by the Faculty of Pure Science, upon the research work done during that period.

D.Sc.—The degree of Doctor of Science may be conferred upon any Master of Science of not less than five years' standing from the date of his admission to the degree of Bachelor, provided that he has published, in recognised journals or transactions, a research or researches of special merit and approved by the Faculty of Pure Science as qualifying him for the degree.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Three hours per week, £3 3s.; Six, £5 5s.; Nine, £7 7s.; Twelve, £9 9s.; Eighteen, £12 12s.; Twenty-four, £14 14s.; Thirty-two, £16 16s.; Honour or University Students taking eighteen hours or more per week, £12 12s.

Students joining the Laboratory for one term are charged one-half, and for two terms two-thirds of the Fees for the whole Session.

A Course of Lectures, with a special class in Laboratory Work, is arranged for Medical Students entering for the Conjoint Board Examinations. Fee, £7 7s.

A course of Practical Chemistry which meets the requirements of candidates for the Diploma of Public Health is held during the Michaelmas and Lent terms. Fee, £6 6s.

An arrangement has been entered into with the Board of Education, London, S.W., which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Board being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar of the University.

Evening Classes.—Lecture Class and Laboratory, on Thursday evening during the Michaelmas and Lent terms. Fee, £1 10s.

DEPARTMENT OF METALLURGY.

Professor—J. O. Arnold, D.Met., F.R.S.

Senior Lecturers—F. K. Knowles, B.Met.; F. Ibbotson, B.Met., B.Sc.

Lecturer—J. H. Wreaks, B.Met.

Demonstrators—L. Aitchison, M.Met.; E. C. Glanet, Dr. Ing.; F. C. Thompson, B.Sc., M.Met.

Lecturer in Non-ferrous Metallurgy—G. B. Brook.

Demonstrator—F. Orme, B.Met.

Lecturer in Electro-metallurgy—W. R. Barclay, A.M.I.E.E.

This Department has been equipped to meet the require-

ments of the local industries. The Laboratory is fitted with the most modern apparatus for metallurgical analysis, more especially with appliances for the rapid and accurate chemical examination of iron and steel, fuel, and refractory materials. It also contains a complete pyrometric installation, and a laboratory for the study of the micrographic analysis of metals fully equipped with specially designed microscopes by Ross, polishing tables, etching appliances, incandescent light for evening work, &c. The Department is now most complete for teaching the practical manufacture, the chemical constitution, and the physical properties of steel. Special attention is given to the determination of the microscopic constituents of steel. Although the chief industry of the district occupies the central position in the course of instruction, general metallurgy is dealt with in the Non-ferrous Department described below. Students are thus enabled to select and at once enter upon a course of scientific metallurgical training of immediate practical utility. They may take up and work through any portions of the course, but certificates are granted only to those who follow the prescribed courses and pass the necessary examinations. Lectures on Iron and Steel Manufacture, on Fuel and Refractory Materials, and Metallurgical Geology. Practical Metallurgy:—Laboratory, Furnaces, Foundry, and Testing Machine Course; Practical Course of Metallurgy other than Iron and Steel; Practical Fuel Course for Students in Collieries or Gas Works.

A steel works has been erected in connection with the Sheffield University at a cost of about £15,000, with a most varied and complete plant. The most recent addition to the steel works plant is a 3 cwt. Kjellin induction furnace worked by a 120 H.P. Motor-generator set with two-phase current. The Metallurgical Department of Sheffield University is "in association" with the Royal School of Mines for teaching the advanced metallurgy of Iron and Steel.

There has been recently added to the curriculum Day and Evening courses in Electro-metallurgy and Non-ferrous Metallurgy. The Electro-metallurgical Laboratory is completely equipped for the practical study of every branch of the art of the Electro-deposition of metals, special attention having, however, been paid—in the selection and arrangement of plant and apparatus—to the specific requirements of the Sheffield trades. The plant and machinery is thoroughly up-to-date in character. Working accommodation is provided for 30 students at one time, and the course extends over three university years.

The Non-ferrous Department has been established to meet the needs of the lighter Sheffield trades of Silver and Electro-plate, Brass, and allied industries. It is completely equipped for dealing with every phase of the work from the raw material. The melting shop is fitted with furnaces capable of dealing with casts up to 70 lbs. weight, so that commercial practice can be followed. Two large laboratories, the one with 32 places for preparatory students, the other with accommodation for 40 advanced students, provide the means for the chemical examination of the alloys prepared. A Staff and Post-graduate research laboratory completes the provision for the chemical side of the work. The Micrographic Laboratory is equipped with a complete Zeiss Photo-micrographic camera, direct driven polishing blocks, and Ross microscopes. The recalcence laboratory for the estimation of temperatures during melting, annealing, or other heat treatment has a complete pyrometric installation. An Arnold and Colver-Glaucet Pyrometer permits of readings every 1° C. up to 1300° C. Facilities are provided for observing the thermal changes *in vacuo*. The Chronographic recorder is served by electric or coke furnaces, and the installation may be regarded as the most complete of its kind.

Degrees are awarded to successful students in Steel Metallurgy, and Associateships in both Steel and Non-ferrous Metallurgy.

UNIVERSITY COLLEGE, READING.

Professor of Chemistry—H. Bassett, D.Sc., Ph.D., D. ès Sc., F.I.C.

Lecturers—J. W. Dodgson, B.Sc.; A. E. Everest, D.Sc., Ph.D.

Professor of Agricultural Chemistry—S. J. M. Auld, D.Sc., Ph.D., F.I.C.

Research Chemist in Dairying—J. Golding, F.I.C.

Lecturer in Agricultural Chemistry—J. A. Murray, B.Sc.

The lectures and laboratory work are so arranged as to be suitable for students preparing for the London B.Sc. (Pass or Honours), or for the College or other Diplomas in Agriculture, Horticulture, or Dairying. There is a general course of Intermediate standard, also another suitable for first year students of Agriculture and Horticulture. In their second and third years Science students attend special lectures in Inorganic, Organic, and Physical Chemistry, while Agricultural students take special courses under the Professor of Agricultural Chemistry. The laboratories are well equipped for all branches of practical work.

Halls of Residence—(Men) Wantage Hall, St. Patrick's Hall; (Women) St. Andrew's Hall, Wessex Hill, St. George's Hostel.

Full details of fees, scholarships, &c., can be obtained from the Registrar.

UNIVERSITY COLLEGE, DUNDEE.

UNIVERSITY OF ST. ANDREWS.

Professor of Chemistry—Alex. McKenzie, M.A., D.Sc., Ph.D.

Lecturer—J. K. Wood, D.Sc.

Demonstrator—S. C. Bate, B.Sc., A.I.C.

Lecture Assistant and Lab. Steward—J. Foggie, F.C.S.

The Session consists of three Terms:—The Martinmas Term begins early in October and ends before Christmas; the Candlemas Term begins early in January and ends about the middle of March; the Whitsunday Term begins in the middle of April and ends at the end of June.

Three Courses of Lectures are given, each extending through all three terms. The General Course, meeting four or five days a week (including Tutorial Meetings), is intended for beginners, and qualifies for Graduation Examinations in Arts (M.A. General), Science (First B.Sc.), and Medicine (First M.B., Ch B).

The Special and Honours Courses, each meeting twice or thrice weekly, qualify for Degree Examinations in Arts (Special and Honours, respectively), and in Science (Final B.Sc. on Intermediate and Higher Standard, respectively).

All three are General Courses, including Inorganic, Physical, and Organic Chemistry.

The Laboratories are well equipped, and instruction is provided for students in Arts, Science (Pure and Applied), Medicine (including Public Health); provision is also made for students desiring to undertake Research.

UNIVERSITY OF ABERDEEN.

CHEMISTRY.

Professor—Frederick Soddy, M.A., F.R.S.

Lecturer on Physical Chemistry—Francis W. Gray, M.A., D.Sc.

Demonstrators—Joseph Knox, D.Sc.; W. H. T. Williamson, B.Sc.; James D. Pratt, M.A., B.Sc.

I. *General Lecture Course* (100 Lectures).—Daily during the Winter Session. The subjects treated of include (1) The Laws of Chemical Combination and the General Principles of Chemistry; (2) Non-metallic and Metallic Elements, and their Compounds; (3) Organic Chemistry; (4) Applications of Chemistry to the Arts and Manufactures. Fees, for first attendance, £4 4s.; for subsequent attendance, £3 3s. A Tutorial Class (without fee), conducted by the Junior Demonstrator, is held in connection with this course.

II. *Practical Course for Beginners*.—In connection with the preceding course a practical course is obligatory.

It is held during the Spring Term, and occupies seven hours a week, seventy hours in all. It consists of exercises in practical methods, preparations, volumetric and qualitative analysis, and the identification of some organic compounds. Fee, £3 3s.

III. *Physical Chemistry* (60 Lectures).—Three Lectures a week on Physical Chemistry, with Practical Demonstrations, are delivered during the Winter Session by the Lecturer, Dr. F. W. Gray. Fee, £2 2s.

IV. *Inorganic Chemistry* (40 Lectures).—Two Lectures a week on Advanced Inorganic Chemistry are delivered during the Winter Session by the Lecturer, Dr. J. Knox. Fee, £2 2s.

V. *Special Lecture Course on Organic Chemistry* (50 Lectures).—Daily during the Summer Session. Fee, £3 3s.

VI. *Chemical Laboratory*.—The Laboratory is open to Students daily from 9 a.m. to 5 p.m. Each Student on entering is allowed to arrange his hours of work so as to suit his own convenience, but must adhere to these hours when once fixed. The Laboratory instruction includes: (1) General experiments; (2) Preparations; (3) Qualitative analysis; (4) Quantitative analysis: gravimetric, volumetric, and gasometric. The Course qualifies for the examinations of the Institute of Chemistry. Fee, £3 3s. a session. A certain number of free places are available, on the recommendation of the Professor, and subject to the approval of the Senatus, for research students.

UNIVERSITY OF ABERDEEN AND ABERDEEN AND NORTH OF SCOTLAND COLLEGE OF AGRICULTURE.

Agricultural Chemistry and Forest Chemistry.

Professor—James Hendrick, B.Sc., F.I.C.

Assistants—R. Glegg, B.Sc., F.I.C.; Arthur E. M. Smith, M.A., B.Sc.

I. *Preparatory Courses in General Chemistry and in Organic Chemistry* are given for those who are unable to take the full University Courses in these subjects. The course in General Chemistry consists of about sixty Lectures with Practical Work (seven hours weekly) during the Winter Session. The course deals with the general principles of Chemistry, and with those parts of Inorganic Chemistry which are of more immediate concern to students of Agricultural Chemistry. The Practical Work goes along with and illustrates the Lectures. Fee, £4 4s.

The course in Organic Chemistry consists of about thirty Lectures, and about thirty hours practical work, and is given during the Summer Session. It deals especially with those parts of the subject which are directly related to Agricultural Chemistry. Fee, £2 2s.

II. *Agricultural Chemistry (General Course)*.—This class meets daily during the Winter Session, and includes both Lectures and Laboratory Work. The Lectures deal with the Chemistry of the Atmosphere, the Soil, Manures, Foods, Preservatives, Insecticides, &c. The Physiological Chemistry of Plants and Animals, the Composition and Manurial Requirements of Crops, and Dairy Chemistry are also treated of. The Laboratory Work is primarily intended to accompany and illustrate the Lectures. Exercises dealing with the properties and composition of Soils, Manures, Feeding-stuffs and Waters, and with the impurities and adulterations of these, occupy much of the time given to Practical Work. The fee for the whole Course (Lectures and Practical Work) is £4 4s.

III. *Forest Chemistry (General Course)*.—Students in Forestry take the greater part of the General Lecture Course in Agricultural Chemistry, with special lectures on the Chemistry of Timber and Forest Products. The early part of the Laboratory Work is the same as in the case of Agricultural Students, but the latter part is occupied with special exercises on Forest Products. Fee, £4 4s.

IV. *Laboratory*.—A Summer Course in Practical Chemistry is given to prepare students who have not previously done sufficient laboratory work for the course in Agricultural Chemistry or Forest Chemistry. Fee, £2 2s.

V. The Laboratory is open daily from 9 a.m. to 5 p.m.

for students who wish to study the principles and practice of Agricultural Chemistry or Forest Chemistry, or to undertake research in these subjects.

UNIVERSITY OF EDINBURGH.

DEPARTMENT OF CHEMISTRY.

Professor—James Walker, LL.D., D.Sc., Ph.D., F.R.S.
Lecturers—L. Dobbin, Ph.D.; A. C. Cumming, D.Sc.; J. E. Mackenzie, Ph.D., D.Sc.; J. P. Longstaff, D.Sc.; S. A. Kay, D.Sc.; and H. G. Rule, B.Sc., Ph.D., and Demonstrators.

The three working terms are each of ten weeks' duration, viz.:—Autumn term, October to December; Spring term, January to March; Summer term, April to June.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical students is given. The class meets daily; fee, £4 4s. The First Course for Arts and Science students meets three times a week throughout the year; fee, £4 4s. The Second Course is given on Organic, Advanced Inorganic, and Physical Chemistry. The class meets three times a week throughout the year; fee, £4 4s. Tutorial Classes are held in connection with the First and Second Courses. All Arts and Science Classes are open to Women Students.

In addition to the above, Advanced Lecture Courses are given on particular branches of Physical, Organic, and Inorganic Chemistry.

Laboratories.—Practical classes for Medical Students meet during the Winter Session and in the Summer Session. (Fee, £3 3s.). The Elementary Laboratory course for Arts and Science students is held for four hours per week during the year. Fee, £4 4s. The advanced laboratories for Science and Arts Students engaged in analytical and advanced practical work are open daily from 9.30 till 4.30. Fees: Whole Day—Year, £16 16s.; one term, £6 6s. Half Day—Year, £8 8s.; one term £3 3s. Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry (including Gas Analysis, Physico-chemical Measurements, and Assaying). Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical language, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (i.e., Zoology and Botany), Natural Philosophy, and Chemistry. The Final B.Sc. Examination in Pure Science includes any three or more of the following subjects:—Mathematics, Natural Philosophy, Astronomy, Chemistry, Human Anatomy (including Anthropology), Physiology, Geology (including Mineralogy), Zoology (including Comparative Anatomy), and Botany (including Vegetable Physiology). In the Final Examination two written papers are set in each subject professed, the second of a higher standard than the first. Candidates must pass the first section in all, and the second section in at least one, of the subjects professed; the same regulations apply also to the Practical and Oral Examinations. Chemistry in this examination embraces Inorganic Chemistry, Organic Chemistry, and Physical Chemistry. Practical Examination:—

Complex Qualitative Analysis; Preparations; Gravimetric and Volumetric Analysis; Testing of Organic Substances. Each candidate taking the higher standard will also be examined on Ultimate Organic Analysis; Gas Analysis; Assaying; and Physico-chemical Measurements.

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry may be required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Principal—A. P. Laurie, M.A., D.Sc., F.R.S.E.

Assisted by the following Lecturers and Demonstrators:—A. Archibald Boon, B.A., D.Sc.; Andrew King, F.I.C.; F. D. Miles, B.Sc.; and Clerk Ranken, D.Sc.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

An extensive range of new Chemistry Laboratories, embodying the most modern developments in laboratory design and equipment, and including a complete plant for the production of liquid air, has recently been built. The Chemistry Courses are designed to meet the requirements of Analytical and Technical Chemists. The College is a recognised training centre for the examinations of the Institute of Chemistry, and students can obtain the necessary instruction in General Chemistry, and also the specialised instruction required for the Final Examination for the Associateship of the Institute in the departments of Organic Chemistry, Metallurgy, Foods and Drugs, and Bio-chemistry.

The course for the Diploma of the College has been laid down on the same general lines as that required for the examinations of the Institute of Chemistry.

The Chemistry Courses are recognised by the University of Edinburgh as qualifying courses for the B.Sc. degree.

A Laboratory, under the charge of Prof. Emil Westergaard, has been provided for the study of Technical Mycology of Brewing, Distilling, Yeast Manufacture, Maltng, Butter, Margarine, and Cheese Manufacture, Agriculture, Starch, Sugar, Preserve Making, &c. In this laboratory provision is made for the teaching of Biology, and the microscopic examination of Foods and Drugs, in connection with the examinations of the Institute of Chemistry.

Day Classes open on October 12th, and the Evening Classes on September 30th.

Matriculation Fee, 5s.; Composition Fees from £15 15s. to 21 guineas per annum. Full particulars are published in the Calendar of the College, which is issued early in September.

THE ROYAL TECHNICAL COLLEGE, GLASGOW.

Professor of Chemistry—G. G. Henderson, D.Sc., M.A., LL.D., F.I.C.

Professor of Technical Chemistry—T. Gray, D.Sc., Ph.D.
Lecturer on Dyeing—A. B. Steven, B.Sc.

Lecturer on Sugar Manufacture—T. H. P. Heriot, F.C.S.

Professor of Metallurgy—A. Campion, F.I.C., F.C.S. Also, Professors and Lecturers in the other leading branches of Pure and Applied Science and Technology.

Session opens September 28th, 1915.

The main object of this College is to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade. It was founded by an Order in Council, dated November 26th, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College

(established 1796), the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments. The diploma course in Chemistry extends over four years.

Students who have matriculated at the University of Glasgow can qualify for the degree of B.Sc. in Applied Science by a tondance on the Day Classes of the College.

Complete courses of instruction are provided in both Day and Evening Classes.

Copies of the Calendar for 1915-1916 may be had from the Director, Mr. H. F. Stockdale,; price by post, 1s. 4d. Prospectuses will be sent free.

UNIVERSITY OF ST. ANDREWS.

UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD

Professor of Chemistry—James C. Irvine, Ph.D., D.Sc. The Session begins on October 11th. A Competitive Examination, open to intending Students of Arts, Science, and Medicine, for about thirty-six Bursaries, ranging in value from £50 to £10 each per annum, is held annually in June. (For 1916 entries are due May 23rd). One of these is open to Men or Women, and fifteen are restricted to Women, nine of the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine. The remainder are open to men only.

A Hall of Residence is provided for Women Students. Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree, and the M.B., Ch.B. Degrees; the regulations will be found in the "University Calendar."

Lecture Courses.

Three distinct Courses of Lectures are given, each extending over the three terms of the academc year.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment.

This course of instruction is intended to meet the requirements of the M.A., First Science, and M.B., Ch.B. Exams., so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part to General and Physical Chemistry, the instruction in general being such as is required for the Final Science Exam. on the Lower Standard and the Special Exam. for the M.A. Degree.

Third Year's Course.—Short courses of lectures on selected topics are given to Students preparing for the B.Sc. on the Higher Standard or the M.A. Degree with Honours.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £4 4s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis; (3) Practical Physical Chemistry. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the Exams. in Arts, Science, and Medicine.

The fee for the Ordinary Course of Practical Chemistry is £3 3s, and for the Advanced Course £10 10s.

Original Research.

A special Research Department has been instituted by the University, the laboratories of which are open to students who give proof of their capacity to conduct original investigation. Graduates of other Universities who spend two years in the laboratory as Research Students are eligible for the D.Sc. degree of the University, and special chemicals and apparatus are provided free of charge. Graduate workers can also qualify for the Berry, 1851 Exhibition, and Carnegie Research Scholarships or Fellowships.

Students may work either independently or in collaboration with the Professor, to whom all communications should be addressed.

QUEEN'S UNIVERSITY, BELFAST.

Professor—E. A. Letts, Ph.D., D.Sc., F.R.U.I., &c.

Lecturer on Organic Chemistry—A. K. Macbeth, D.Sc.

I.—Chemistry.—The lectures are delivered at 12 o'clock on the first five days of each week, and terminate about the end of March. The course embraces the elements of Physical, Inorganic, and Organic Chemistry. Fee, £3 3s.

II.—Advanced Chemistry.—Inorganic and Organic. The lectures are given at such days and hours as suit the convenience of the class. Fee, £2 2s.

III.—Practical Chemistry.—In this course the Students are instructed in the general methods of Qualitative and Quantitative Analysis, Inorganic preparations, &c. The class is held on four days in the week during the second term for two hours each day. Fee, £3 3s.

IV.—Practical Chemistry for Engineering Students.—A special course is given during the first term. Fee, £3 3s.

V.—Laboratory Pupils.—The Chemical Laboratories are open from the second week in October to the beginning of July, on the first five days of the week, from 10 a.m. —5 p.m. (except during the vacations). Students are admitted as working pupils on payment of a fee of £3 3s. for one term, £5 5s. for two, or £7 7s. for the whole Session. Facilities are provided for Students who wish to undertake research work.

Scholarships.—The following College Scholarships are awarded specially in connection with the schools of Chemistry and Physics:—Post Graduate Scholarships in Chemistry alone awarded annually of £50, and tenable for one year. Andrews Studentship in Chemistry and Physics, value about £80 annually, and tenable for two years. 1851 Exhibition Scholarships: One of these Scholarships has hitherto been placed at the disposal of the College every two years, of the annual value of £150, tenable for two or under special conditions for three years, and also one of the Industrial Bursaries.

UNIVERSITY COLLEGE, CORK.

A CONSTITUENT COLLEGE OF THE NATIONAL UNIVERSITY OF IRELAND.

Professor—Augustus Edward Dixon, M.D.

Assistant Lecturer—John Taylor, M.Sc.

Demonstrator—H. R. S. Clowthry, B.Sc.

The College Session will commence in October, 1915,

and end in June, 1916. All classes are open to male and to female students.

The following courses are provided:—

1. First Year Course for B.Sc.—General and Elementary Physical Chemistry, Inorganic Chemistry, Introductory Organic Chemistry, Practical Chemistry.
2. Second Year Course for B.Sc.—Advanced Inorganic Chemistry, Advanced Organic Chemistry, Practical Chemistry.
3. Third Year Course for B.Sc.—Physical Chemistry, Advanced Organic Chemistry, Practical Chemistry.
4. Courses in Systematic and in Practical Chemistry for students of Medicine proceeding to the Degrees of the University, or to the Examinations of the Medical Licensing Bodies of Dublin and of Edinburgh.
5. Courses in Systematic and in Practical Chemistry for Students of Engineering.
6. Laboratory Practical Course for the Diploma in Public Health.

Full particulars as to Lectures, Fees, Scholarships, Exhibitions, &c., are contained in the Regulations extracted from the College Calendar, which will be supplied on application to the Registrar.

NATIONAL UNIVERSITY OF IRELAND.

UNIVERSITY COLLEGE, GALWAY.

Professor—Alfred Senior, Ph.D., M.D., D.Sc., F.I.C., F.C.S., M.R.I.A.

Demonstrators—Robert B. Forsier, Ph.D., and Miss R. Clarke, B.A., D.Sc.

The Session commences in September and ends in June.

Faculty of Science.—1. *First Year's Courses.*—Laboratory: Inorganic preparations, simple quantitative and simple qualitative determinations. Lectures: A study of the chief non-metallic elements, their reactions and compounds, the molecular and atomic hypotheses, the leading metals, and an elementary consideration of the constitution and reactions of typical fatty and aromatic organic compounds. 2. *Second Year's Courses.*—Laboratory: Organic preparations, complex qualitative and quantitative inorganic determinations. Lectures: Advanced inorganic and organic chemistry. 3. *Third Year's Courses.*—Laboratory: Qualitative and quantitative organic determinations, molecular weight determinations, gas analysis, thermo-electro and photochemical and other physical determinations. Lectures: General, physical, inorganic, and organic chemistry, a detailed study of special branches, and the historical development of chemistry.

Faculty of Arts.—*First Year's Course.*—Same as Faculty of Science.

Faculty of Medicine.—*First Year's Courses.*—Laboratory: Same as in Faculty of Science, but less detailed, and including the detection of the chief alkaloids, glucosides, and carbohydrates. Lectures: Same as in Faculty of Science, first year.

Faculty of Engineering.—*First Year's Courses.*—Laboratory: Same as in Faculty of Science, but less detailed, and including a special study of metals, alloys, and other materials used in building construction, also determination of hardness in waters. Lectures: Same as in the Faculty of Science, but not including organic chemistry.

The College offers a Scholarship in Chemistry for competition in alternate years of the value of £60, and Chemistry enters into the subjects required for numerous Scholarships in the Faculties of Science, Medicine, and Engineering. The Royal Commissioners for the Exhibition of 1881 offer every two years a Science Research Scholarship of £150 per annum. This Scholarship has already been held by six Chemistry Students of this College.

For details as to Fees, Regulations as to Scholarships, and other particulars apply to the Registrar, from whom the Calendar and other College publications may be obtained.

ROYAL COLLEGE OF SCIENCE, DUBLIN.

The Royal College of Science supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the Schools of Science.

Diplomas are awarded in the Faculties of Engineering (Mechanical and Electrical), Applied Chemistry, and Agriculture. If accompanied by a certificate from the Professor of Chemistry, the Diploma of Associate of the Royal College of Science in the Faculty of Applied Chemistry is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the final practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Inorganic Chemistry, Elementary and Advanced; (2) Organic Chemistry, Elementary and Advanced; (3) Analytical and Experimental Chemistry; (4) Physical Chemistry; (5) Metallurgical and Technological Chemistry and Assaying; (6) Instruction in Chemical Research.

Fees payable by Non-Associate Students:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£5 for three months; £9 for six months; £12 for the entire session. Assaying—£5 for three months; £9 for six months. £12 for the entire session.

There are six Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for three years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College.

A limited number of Scholarships and Teacherships in Training in Science and Technology are competed for each year. These Scholarships are of the value of £50 a year for four years, and, in addition, entitle the holder to free instruction during the full Associateship Course.

For further particulars apply to the Registrar.

PROFESSIONAL CHEMICAL QUALIFICATION (F.I.C. AND A.I.C.).

THE INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.—The Institute of Chemistry was founded in October, 1877, and incorporated by Royal Charter in June, 1885, to maintain the efficiency and integrity of the profession of Chemistry, including professional consulting and technological chemists, public analysts, and chemical advisers. *The Studentship.*—Every Candidate for admission to the Studentship is required to produce evidence that he is at least seventeen years of age, and that he has passed a Preliminary Examination in subjects of general education, recognised by the Council of the Institute. He must also show that, at the time of making application for registration, he is working at a College or University recognised by the Council, or under the direction of a Fellow of the Institute in an approved laboratory. *The Intermediate Examination in General Theoretical and Practical Chemistry.*—Candidates for admission to the Intermediate Examination (Fee, £5 5s.) are required to produce evidence (I.) of having passed an approved Preliminary Examination in subjects of general education; (II.) of having regularly attended systematic day courses, in a College or University recognised by the Council, during at least three academic years, in theoretical and practical Chemistry, and courses in Physics, Elementary Mathematics, and one of the following subjects, in accordance with the Regulations of the Institute: (i.) Higher Physics; (ii.) Advanced Mathematics; (iii.) Mechanics and Chemical Engineering; (iv.) Metallurgy; (v.) Geology and Mineralogy; (vi.) Physiology; (vii.) Bacteriology; (viii.) Agriculture; (ix.) Elementary Botany; (x.) Elementary Biology; and (III.) of having satisfactorily passed the Class Examinations in all the subjects required to be taken. As an alternative in the matter of training (II.), a candidate may take two years' day courses in a recognised Institution as indicated above, and work systematic

ally for two other years under a Fellow of the Institute in an approved laboratory. A Candidate who has taken a Degree in Science (including Inorganic and Organic Chemistry, and Physics in the Degree Examination, Mathematics having been also taken at either the Final or Intermediate University Examination) in a University recognised by the Council, is eligible for admission to the Intermediate Examination of the Institute. Holders of certain Honours Degrees or Diplomas are exempt from passing the Intermediate, and, by virtue of the qualifications, are eligible for admission to the Final Examination direct. A Candidate who has passed the Intermediate Examination of the Institute, or who is entitled to claim exemption from passing the Intermediate Examination, is eligible for admission to the Final Examination. *The Final Examination* (Fee, £5 5s.) *for the Associate ship (A.I.C.).*—This comprises, in addition to a general knowledge of all branches of chemistry, a thorough knowledge of one branch—Mineral chemistry; metallurgical chemistry; physical chemistry; organic chemistry; chemistry (including microscopy) of food and drugs, fertilisers and feeding-stuffs, soils, and water; or biological chemistry. All Candidates for the Final Examination are required to translate French and German technological literature, with the aid of dictionaries. Candidates taking the food and drugs section must take a course in botany, and those taking biological chemistry a course in biology. *Fellowship (F.I.C.).*—For admission to the Fellowship, an Associate is required to have been registered for three years, and to have been continuously engaged during that period in the study and practical work of applied chemistry in a manner satisfactory to the Council.

Full particulars are given in "The Book of Regulations for the Admission of Students, Associates, and Fellows," which may be obtained (gratis) from the Registrar, 30, Russell Square, London, W.C. Past Examination Papers, Annual Sets, 6d. each.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

CITY AND GUILDS OF LONDON INSTITUTE—The operations of the Institute are divided broadly into four branches:—(1) The City and Guilds (Engineering) College, (2) the City and Guilds Technical College, Finsbury, (3) the City and Guilds South London Technical Art School, and (4) the Department of Technology of the Institute. Technological Examinations are conducted once every year at various centres throughout the kingdom. Programmes of the respective Colleges may be had on application. *City and Guilds (Engineering) College, Exhibition Road.*—The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of productive industry, whether Manufactures or Arts. The main purpose of the instruction given is to practically demonstrate the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons training to become Technical Teachers; 2. Persons preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. *City and Guilds Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations

of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in the various special subjects. *South London Technical Art School.*—Classes in Modelling, Design, Drawing and Painting.

CITY OF LONDON COLLEGE, White Street, Moorfields.—A. W. Bain, B.A., B.Sc., F.I.C., and Assistants. Classes and Laboratory Practice in Chemistry, Botany, and Geology, open to Students of both sexes. Courses on Commercial Products—Oils, Tea, Timber, Textiles. Session commences Sept. 27.

THE POLYTECHNIC, Regent Street, W.—Frank E. Weston, B.Sc., F.C.S., and Assistants. General, Technical, and Applied Chemistry. Gas Manufacture and Analysis, Paints and Varnishes, Oils and Fats, Dairy Products, Conjoint Board Chemistry, Chemistry for Insurance Surveyors. Special research laboratory. Session commences Sept. 27.

BATTERSEA POLYTECHNIC.—Principal, F. H. Newman. M.A., Ph.D. Inorganic, Organic, and Technological Chemistry, John Wilson, M.Sc. (Vit.), F.I.C., and Assistants. Complete courses of Instruction are given in Chemistry (Inorganic and Organic), together with Physics, Electricity, Engineering subjects, Analysis of Foods, Bacteriology, Materia Medica, Paper Making and Testing, Oils and Fats, Toilet Soap Manufacture, Waxes and their Products, Petroleum and its Products, Dyeing and Cleaning, Gas Analysis, &c., for intending technological and works chemists. Certain of the Courses (Day and Evening) are recognised by the University of London in preparation for the B.Sc., for which examination (Pass and Honours) complete courses of instruction, under recognised teachers, are provided. Special Evening Courses in various Technical subjects. (For further information see College Calendar).

BOROUGH POLYTECHNIC INSTITUTE, 103, Borough Road, S.E.—Chemistry Department under the Direction of C. Doré, M.A., D.Sc. Evening Lectures and Laboratory Work in Inorganic and Organic Chemistry. Special Lectures and Laboratory Courses in Electro-chemistry and Electro-chemical Analysis. Special Courses of Lectures on various Technical subjects. (For further information see College Calendar).

BIRKBECK COLLEGE, Breams Buildings, Chancery Lane.—Chemistry Courses conducted by G. Senter, D.Sc., Ph.D. (assisted by G. W. Clough, B.Sc., F. Barrow, M.Sc., G. Martin, D.Sc., and Maude O. Newling, B.Sc.), prepare for various Examinations, the B.Sc. and M.B. Degrees of the London University, Conjoint Board, Pharmaceutical Examinations, Board of Education, &c. The Session will commence on Monday, Sept. 27. The Day and Evening courses of study include Chemistry, Physics, Botany, Zoology, Geology, Mathematics, Latin, Greek, Modern Languages, Economics, Geography, Logic, History, and various branches of Law. All the Courses are conducted by recognised teachers of the University and provide for the Examinations of the University of London. The Calendar supplies detailed information respecting the Courses of Study, Examinations, &c.

NORTHERN POLYTECHNIC INSTITUTE, Holloway Road, N.—Principal, R. S. Clay, D.Sc. Instruction in theoretical and practical Inorganic and Organic Chemistry. Systematic Day and Evening Courses for the London University Degrees, Pass and Honours, also for the Board of Education examinations. Prospects sent free on application to the Secretary.

NORTHAMPTON POLYTECHNIC INSTITUTE, St. John Street, E.C.—Principal, R. Mullineux Walmsley, D.Sc.,

&c. Classes in Electro-chemistry, Electro-plating, Engineering Chemistry, Electro-metallurgy, Electrotyping, Stereotyping, and Metal Colouring. (For full details see Prospectus). Telephone, Holborn 1194.

SOUTH WESTERN POLYTECHNIC INSTITUTE, Manresa Road, Chelsea.—This Institute offers facilities for academic and technical education in many branches of Chemistry and Metallurgy. The department has designed both day and evening courses to meet the many requirements of these professions in London. Complete courses in General Chemistry, Metallurgy, and Assaying requisite for the B.Sc. and A.I.C. Examinations, Technical Courses. Ample opportunity for individual work has been arranged for both day and evening students. A full list of these courses will be supplied on application. A feature of the laboratory work is the facility given for specialising in any particular branch of the above subjects, thus supplying a much needed want to men who have neither the time nor necessity for attending a degree course. The various lecturers will be pleased to advise intending students with regard to selection of courses. The department is under the control of J. B. Coleman, A.R.C.S., A.I.C., F.C.S., and the Institute desires to make its courses of found practical use to those engaged in Chemical Industries.

EAST LONDON COLLEGE, Mile End Road.—Chemistry: Professor, J. T. Hewitt, M.A., D.Sc., Ph.D., F.R.S.

SIR JOHN CASS TECHNICAL INSTITUTE, Jewry Street, Aldgate.—Principal, Charles A. Keane, D.Sc., Ph.D., &c., assisted by R. S. Willows, M.A., D.Sc., H. J. S. Sand, D.Sc., Ph.D., G. F. Morrell, B.Sc., Ph.D., &c., Arthur R. Ling, F.I.C., C. O. Bannister, A.R.S.M., M.I.M.M., G. Patchin, A.R.S.M., E. M. Boote, Assoc. Inst. C.E., Arthur Harden, D.Sc., F.R.S., &c., J. S. S. Brame, E. C. Snow, M.A., D.Sc., F. J. Harlow, B.Sc., &c. The new Session of the Sir John Cass Technical Institute, which is especially devoted to technical training in Experimental Science and in the Artistic Crafts, will commence on Monday, September 27th. The instruction in experimental Science provides systematic courses in Mathematics, Physics, and Chemistry for London University examinations in addition to the courses on higher technological instruction, which form a special feature of the work of the Institute. In connection with the latter, the curriculum in connection with the Fermentation Industries now includes courses of instruction on Brewing and Malting, Bottling and Cellar Management, Brewery Plant, and on the Micro-biology of the Fermentation Industries. A connected series of lectures dealing with the Supply and Control of Power has also been arranged to meet the requirements of those engaged in works connected with Chemical, Electrical, and the Fermentation Industries. These will comprise a course of 20 lectures on the Supply and Control of Liquid, Gaseous, and Solid Fuel, a course of 5 lectures on Electrical Supply and Control, and a connected course of 5 lectures on the Transmission of Power. In the department of Physics and Mathematics, a special course of Lectures and Demonstrations will be given on Colloids, which will deal with the methods employed in their investigation and their relation to technical problems; also special courses of Lectures on the Influence of Surface Tension on Chemical Phenomena, the Methods of Differential and Integral Calculus, and on the Theory and Application of Mathematical Statistics, the latter of which will treat of the application and modern mathematical methods of dealing with statistical data in social, educational, economic, and physical problems. Opportunity will be given to students to investigate problems on their own account. In the Metallurgy department, in addition to the ordinary courses, special advanced courses are provided on Gold, Silver, and allied metals, on Iron and Steel, on Metallography and Pyrometry, on Heat Treatment of Iron and Steel, on Mechanical Testing of Metals and Alloys, on Mining, Mine Surveying, and on Mineralogy. Full facilities for advanced practical work and research in Chemistry, Metallurgy, and Physics.

EAST HAM TECHNICAL COLLEGE.—Principal, W. H. Barker, B.Sc. Head of Chemical Department—A. E. Dunstan, D.Sc. (Lond.). Lecturers—F. B. Thole, D.Sc.; E. D. Griffiths, B.Sc.; R. W. Wilson, F.C.S. Demonstrators—S. J. Plaice; A. G. Mussell. Chemical Engineering and Gas Engineering—A. J. Nice. Gas Supply—G. Jenkins. Soap Manufacture—C. J. Benedict. Oils, Fats, and Waxes—J. H. Baxter. Tar Distillation, &c.—A. J. Nice and A. E. Dunstan, D.Sc. Metallurgy—F. B. Thole, D.Sc. Sugar Manufacture—A. Wade. Painters' Oils, Colours, and Varnishes—R. A. Phillips. Evening Classes and Secondary School.

BLACKBURN MUNICIPAL TECHNICAL SCHOOL.—Chemistry: Robert H. Pickard, D.Sc. (Lond.), &c., assisted by Jos. Yates, M.Sc., F.I.C., and Hannah de Pennington, B.Sc. Session commences Sept. 27. Full details of the Classes are given in the "Students' Handbook," which may be had at the Institution (price 1d., by post 3d.).

REDRUTH SCHOOL OF MINES (now incorporated in the School of Metalliferous Mining, Cornwall).—Complete courses of Practical and Theoretical instruction are given in Inorganic Chemistry, Assaying, Mineralogy, Blowpipe Analysis, Mine Surveying, Geology, Principles of Mining, Ore Dressing, Mechanical Engineering, &c., for intending Assayers, Mineral Chemists, Mining Engineers, and Surveyors. Practical instruction in Mining given at the Basset Mines, Ltd. Syllabus on application.

MANCHESTER SCHOOL OF TECHNOLOGY (University of Manchester).—The work of the School of Technology includes advanced study and research in various branches of science and technology, and undergraduate courses in the Faculty of Technology, extending over three years and leading to Degrees and Certificates in Mechanical Engineering, Electrical Engineering, Sanitary Engineering, Textile Industries, Printing and Photographic Technology, Architecture, and in the following branches of Applied Chemistry:—General Chemical Technology, Chemistry of Textiles (Bleaching, Dyeing, Printing, and Finishing), Paper Manufacture, Metallurgy and Assaying, Chemical Technology of Brewing, Electro-chemistry, Photography. The provision for the teaching of Chemistry is of an exceptionally complete character. In addition to the laboratories for Inorganic and Organic Chemistry, Metallurgy, Brewing, Bleaching, Dyeing, and Electro-chemistry, an extensive equipment (including machinery and appliances on an industrial scale) for demonstration, experiment, and original research in connection with the Bleaching, Dyeing, Printing, and Finishing, and Paper-making industries is provided in a separate building. A Brewhouse is also equipped on the low gravity principle with a plant of four bushel capacity.

TECHNICAL COLLEGE, SWANSEA.—Principal, W. M. Varley, M.A., D.Sc., Ph.D. Chemistry, E. A. Tyler, M.A.; Metallurgy, H. I. Coe, M.Sc.; Physics, J. C. Kirkman, B.Sc.; Secretary, W. James. Day and Evening Courses in Pure and Applied Chemistry, Chemical Engineering, Metallurgy, and for Pharmaceutical, Medical, and Dental Students. Session opens Sept. 16th.

WOLVERHAMPTON MUNICIPAL SCIENCE AND TECHNICAL SCHOOL.—Principal, J. D. Coales, D.Sc., M.I.E.E.; Inorganic and Organic Chemistry, Th. J. Murray, M.Sc., Ph.D.; Physics, A. T. Harrison, B.Sc.; Botany, Miss O. E. Ashdown, B.Sc. Human Physiology and Hygiene, H. J. Tench, A.R.S.I. Materia Medica and Pharmacy, F. W. Thompson, Ph.C. Day Classes in Chemistry, and Evening Classes in Chemistry, Physics, Botany, French, &c. Special arrangements are made for the requirements of Pharmaceutical and Medical Students and Chemical Trades. Session commences Sept. 13th. For other particulars and programme, apply G. F. Chell, Secretary.

MUNICIPAL TECHNICAL INSTITUTE, BELFAST.—Principal, F. C. Forth, F.R.C.Sc.I. Chemistry, Prof. H. Wren, M.A., Ph.D., D.Sc. Day and Evening Courses.

THE ANALYSIS OF PLATINUM.*

By F. MYLIUS and A. MAZZUCHELLI.

(Continued from p. 107).

4. Process of Qualitative Analysis.

THERE are many trustworthy methods of detecting the constituents of platinum ores, of which there are usually large quantities at one's disposal. But it is quite a different thing when it is a question of showing the presence of small quantities of the metals in an unknown chloride solution—e.g., the nine metals, palladium, platinum, rhodium, ruthenium, iridium, gold, silver, copper, and iron. Qualitative analysis for this purpose has not been much worked out, and the earlier directions of Mylius and Dietz (*Ber.*, 1889, xxxi., 3191) have proved to be inadequate because they presuppose large quantities of the dissolved metal (viz., 1 grm.). The question of the impurities in platinum metals cannot be seriously discussed unless it is possible to detect much smaller amounts—e.g., 1 mgrm. of each of the metals in question—in a common solution.

A priori it is not to be expected that the projected "analytical process" for the detection of so many metals will be very simple. If it should be the case it cannot be supposed that the separation of the single constituents will be very complete. This latter defect is allowable in qualitative analysis, for it is not necessary to make use of the whole quantity of the individual substances in order to recognise them. This incompleteness, which is only to be expected, is detected in every attempt to effect sharp separations.

If the nine metals are dissolved in equal quantities it will be found that some of them can be more readily detected by their characteristic reactions than others. Among the metals which are difficult to detect in these circumstances is platinum, while ruthenium, for example, may be discovered fairly easily. Ruthenium chloride colours the solutions an intense orange-yellow; this coloration, which is hardly affected by reducing agents (unlike that of Ir, Pd, Fe, &c.), affords a means of recognising the presence of ruthenium during the analysis. We shall shortly discuss in full the difficulty of separating ruthenium from the other metals with ammonium chloride.

A better means of detecting it is provided by treatment with sulphuretted hydrogen, which precipitates ruthenium in the cold (like palladium). But the precipitation is only partial; it may be assumed that some of it is converted into lower states of chlorination (e.g., RuCl_2), which react with more difficulty. It is a fact that the filtrate from the black sulphide, after it has originally been decolorised, assumes a beautiful blue coloration, which has long been regarded as characteristic of ruthenium, for it has not been observed with the other platinum metals, though it has been with tungsten, molybdenum, &c.

The formation of this unknown blue substance is obviously connected with the observation that ruthenium solutions are not completely precipitated by sulphuretted hydrogen at room temperature.

We found that the blue liquid is momentarily decolorised by the cautious addition of chlorine water, but even then by repeated treatment with sulphuretted hydrogen it was not possible to precipitate the ruthenium completely as sulphide at room temperature.

It is only from platinum that ruthenium can be separated fairly well by neutralising the solution of the two chlorides with sodium carbonate and oxidising the warmed solution with a limited amount of sodium (hypochlorite (or bromite); the black ruthenium oxide formed can easily be filtered off from the solution containing the platinum. An excess of the oxidising agent readily dissolves it, giving a yellow solution.

Process of Detecting Pd, Pt, Rh, Ru, Ir, Au, Ag, Cu, Fe (1 mgrm. of each) in a Chloride Solution.

Group Precipitation.

I.—The solution is evaporated almost to dryness, diluted with 2 cc. of water, and filtered from dark precipitate.

Precipitate.—Silver chloride.

II.—The filtrate from I. is saturated with powdered ammonium chloride. After one hour it is filtered and the precipitate washed with a little ammonium chloride solution.

Precipitate.—Platinum, iridium, ruthenium double chlorides.

III.—Filtrate II. is evaporated to dryness with 3 cc. of dilute nitric acid. The cold residue is mixed with dilute nitric acid to give a liquid almost saturated with ammonium chloride, so that the easily soluble double chlorides of rhodium, gold, copper, and iron go into solution, while the dark double salts of palladium, iridium, and ruthenium remain behind. They are filtered off and washed with a very little dilute ammonium chloride + nitric acid.

IV.—The filtrate from III. is evaporated to dryness with dilute hydrochloric acid, the residue dissolved in 5 cc. of water with addition of a drop of dilute hydrochloric acid, and the solution rapidly saturated with sulphuretted hydrogen at 18°. The black precipitate is filtered after ten minutes and washed with water.

Precipitate.—Sulphides of gold and copper.

Secondary Separations.

6. The precipitate is washed on the filter with ammonia. A white precipitate in the filtrate on addition of HNO_3 shows silver.

The dark residue in the filter is treated as in 5.

5. After addition of the insoluble residues obtained in the purification 1—6, the ammonium chloride precipitate is heated in hydrogen (finally to a white heat). The metal is extracted with dilute aqua regia and the platinum in the evaporated solution is detected as the yellow platinum ammonium chloride.

The insoluble residue is heated in a little spoon of gold or silver foil with 0.3 grms. of sodium nitrate. Ruthenium goes over into the melt with a yellow coloration, while a blue insoluble residue indicates iridium.

4. The precipitate is dissolved by evaporating with hydrochloric acid and taken up with 3 cc. of water; the solution is saturated with sulphuretted hydrogen in the cold. The brown flakes of sulphide which are filtered off are evaporated with aqua regia. In the solution of the residue palladium is recognised by the precipitate it gives with mercury cyanide,

Any residues containing iridium were treated according to 5.

3. The sulphide precipitate is dissolved in dilute aqua regia and the solution evaporated. The residue is dissolved in dilute hydrochloric acid and extracted with ether.

Gold is recognised by the yellow coloration of the ethereal layer and by the precipitate it gives with sulphurous acid.

From the aqueous layer the sulphide is precipitated with sulphuretted hydrogen, filtered off, washed, and ignited. The residual oxide is extracted with dilute nitric acid. Copper is recognised by the blue coloration obtained on saturating with ammonia. Any residue which is insoluble in nitric acid is to be transferred to 5.

* Zeitschrift für Analytische Chemie, lxxxix., 1.

V.—The red filtrate from IV. (6–8 cc.) is treated for half an hour in the warmth with sulphuretted hydrogen. After boiling, the brown precipitate is filtered off and washed with water.

Precipitate.—Rhodium sulphide.

VI.—The filtrate from V. is boiled, oxidised with nitric acid, and ammonia is added; the brown precipitate of iron oxide is filtered off. On evaporation the filtrate leaves behind ammonium salts, which are completely volatilised on heating.

The unmistakable smell of ozone which always appears in this reaction is a very characteristic test for the presence of ruthenium.

If, however, iridium is present as well as platinum and ruthenium the process is more complicated; the oxidising agent first precipitates a ruthenium oxide containing iridium, then an iridium oxide containing ruthenium, while the platinum does not remain in the solution, but for the most part goes over into the precipitates with the two oxides. Better results are obtained if an excess of oxidising agent is used at once (thus the ruthenium is converted into soluble ruthenate), and the liquid is then warmed with alcohol to effect reduction. Thus a black mixture of iridium and ruthenium oxide is obtained, while the platinum passes into the filtrate. In this case also the tendency of ruthenium, which has often been alluded to, again appears, and it attaches itself to the allied iridium in the analytical separation.

From what has been already said it appears that platinum, which is so easy to recognise by itself, can be detected only with difficulty in a great excess of other platinum metals. Just as the precipitates of platinum (e.g., platinum ammonium chloride) easily carry down with themselves small quantities of impurities of other metallic compounds, it is itself absorbed in any form by foreign precipitates, which greatly influence the process of isolation. Even the extraction of metallic platinum from its iridium alloys by dilute aqua regia is more difficult to carry out completely if other platinum metals (e.g., ruthenium or rhodium) are present.

The sulphur-yellow colour of its ammonium double chloride is characteristic of pure platinum. Owing to the great analogy of the platinum metals in the formation of their double salts it does not appear strange that the ammonium chloride precipitate used to characterise platinum is often orange-yellow (by a very small percentage of iridium).

Based upon the above observations and considerations, we tried different ways of working out our analytical method. Some of them must be explained more fully hereafter. We may first of all point out that a group separation of the noble from the common metals was found neither necessary nor convenient, so that the tedious reduction of the metals by boiling with formic acid, &c., can be omitted.

The accompanying qualitative analytical method is similar to the usual process of mineral analysis in the use of group reactions, which isolates primary precipitates, which are then subjected to secondary separations.

While the group precipitations proceed from silver to iron (I.—VI. downwards) the secondary separations follow the reversed order (1–6 upwards). This makes

2. The sulphide precipitate is dissolved on the filter with hot dilute aqua regia and the solution evaporated. The residue on being warmed with concentrated hydrochloric acid gives a rose red solution, which indicates rhodium. On warming with mercaptan it is precipitated as a yellow precipitate. Only traces of iridium can be present in the filtrate.

1. The precipitate is ignited. After solution in hydrochloric acid the iron is detected as Berlin blue.

Any insoluble residue must be transferred to 5.

it possible to put the residues, which mostly consist of iridium and ruthenium, with the chief amounts of these metals. The separation of these last is the last part of the analysis.

The above method of qualitative analysis is sensitive enough, and the nine metals, of which 1 mgrm. each is present, can be detected with certainty and without difficulty in the original chloride solution. Working with small masses makes it necessary to reduce the volumes of the solutions and the dimensions of the filters considerably in comparison with the ordinary standards in analysis. The problem described here is not to be regarded as one of microchemistry; this would be the case only if one-tenth of a mgrm. were to be detected. With some practice even this would be possible, using the same method, without employing the microscope.

(To be continued).

WELSH NOTES.

(By Our Special Correspondent).

THE Swansea Vale Spelter and Zinc Smelting Works, which were erected and until quite recently controlled by certain Germans, have now been taken over and will henceforth be under the control of an entirely English group, with the consent and approval of the British Government. These works, which are quite new and arranged upon the most modern principles, will now be immediately enlarged upon an extensive scale, and I understand that it is intended to encourage the development of zinc ore deposits of Great Britain.

The head of the group is Mr. R. Tilden Smith, who is associated with many important enterprises, including the zinc mines of Burma, from which he intends to obtain his supplies of metal. The plant is a facsimile of those which the Germans have erected in Germany, Belgium, and France, and was one of the links in the organisation which enabled them to dominate the zinc market in Europe.

UNIVERSITY OF BIRMINGHAM.

ASSISTANT LECTURER AND DEMONSTRATOR
IN CHEMISTRY.

The Council invites applications for the above
Post. Stipend £150 per annum.

Applications accompanied by testimonials, should be sent to the undersigned not later than SATURDAY, the 18th SEPTEMBER, 1915. No special form of application is required.

The Candidate elected will be required to enter upon his duties on October 1st.

Further particulars may be obtained from—

GEO. H. MORLEY, Secretary.

LEEDS UNIVERSITY.

DEPARTMENTS OF
CHEMISTRY and APPLIED CHEMISTRY.

CHEMISTRY	Professor ARTHUR SMITHELLS, B.Sc., F.R.S.
ORGANIC CHEMISTRY	Professor JULIUS B. COHEN, B.Sc., Ph.D., F.R.S.
PHYSICAL CHEMISTRY	Lecturer—HARRY M. DAWSON, Ph.D., D.Sc.
TINCTORIAL CHEMISTRY and DYEING	Professor ARTHUR G. GREEN, M.Sc., F.I.C., F.R.S. Lecturer —ARTHUR G. PERKIN, F.R.S.
LEATHER INDUSTRIES	Emeritus Professor H. R. PROCTER, D.Sc.
COAL-GAS and FUEL INDUSTRIES, with METALLURGY	Professor JOHN W. COBB, B.Sc., F.I.C.
AGRICULTURAL CHEMISTRY and DISTILLERY	Professor CHARLES CROWTHER, M.A., Ph.D.

The Courses of study are arranged to meet the requirements of Students preparing for the Degrees and Diplomas of the University in any of the above subjects. They also qualify for the Examinations of the Institute of Chemistry.

The next SESSION, 1915–16, begins on FRIDAY, OCTOBER 1st.

Further particulars may be had on application to the SECRETARY.

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BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

MANCHESTER, 1915.

INAUGURAL ADDRESS OF THE PRESIDENT,

Prof. ARTHUR SCHUSTER, D.Sc., Sc.D., LL.D.,
Dr.ès.Sc., F.R.S.

The Common Aims of Science and Humanity.

UNDER the influence of the diversity of pursuits imposed upon us by the conditions of modern life, different groups of the community—men of business, men of science, philosophers, or artists—have acquired detached and sometimes opposing interests. Each group, impressed by the importance of its own domain in the life of the nation, and focussing its vision on small differences and temporary rivalries, was in danger of losing the sense of mutual dependence. But in the shadow of a great catastrophe it has been brought home to us that the clash of interests is superficial, and the slender thread of union which remained has grown into a solid bond. What is the fibre from which the bond is twined? Patriotism may express its outward manifestation, but its staple is the mental relationship which remains continuous and dominant even in normal times, when each of us may peacefully go to earn his living and enjoy the course of his intellectual life.

Outwardly the community is divided into heterogeneous elements with mental attitudes cast in different moulds, and proceeding along separate roads by differing methods to different ideals. Yet as we eliminate the superficial, and regard only the deep-seated emotions which control our thoughts and actions, the differences vanish, and the unity of purpose and sentiment emerges more and more strongly. Mind and character, no doubt, group themselves into a number of types, but the cleavage runs across, and not along, the separating line of professions.

Were it otherwise, the British Association could not perform one of its most important functions—a function not, indeed, originally contemplated, but resulting indirectly from the wise and democratic provisions in its constitution, which enabled it to adapt itself to the changing needs of the time. Our founders primarily considered the interests of scientific men; their outlook was restricted and exclusive, both as regards range of subject and membership. In the words of Sir David Brewster, who gave the first impulse to its formation, it was to be “an Association of our nobility, clergy, gentry, and philosophers.”

The meetings were intended to promote personal intercourse, to organise research, to advocate reform of the laws hindering research, and to improve the status of scientific men. The right of membership was confined to those who already belonged to some learned society, and William Whewell, one of the principal supporters of the movement, even suggested that only authors of memoirs published by a learned society should be admitted.* He emphasised this proposal by the recommendation (“Whewell's Writings and Letters,” vol. ii., p. 128) “in some way to avoid the crowd of lay members whose names stand on the List of the Royal Society.” The reform of the Patent Laws and the introduction of an International Copyright were suggested as subjects suitable for discus-

sion, not apparently from the point of view of general advantage, but merely in the interests of one section of the community.

Whatever the objects of the founders of the Association may have been, it is obvious that questions of public importance could not be permanently excluded from meetings the success of which depended on the interest stimulated in the community. The Statistical Section, which owed its origin to the visit, at the first Oxford Meeting (1836), of Quetelet, the Belgian astronomer and economist, was the first to assert itself by engaging in a discussion of the Poor Laws. Whewell deeply resented this violation of academic neutrality:—“It was impossible,” he wrote, “to listen to the Proceedings of the Statistical Section on Friday without perceiving that they involved exactly what it was most necessary and most desired to exclude from our Proceedings” (*loc. cit.*, p. 289), and again:—“Who would propose (I put it to Chalmers, and he allowed the proposal to be intolerable) an ambulatory body, composed partly of men of reputation and partly of a miscellaneous crowd, to go round year by year from town to town and at each place to discuss the most inflammatory and agitating questions of the day?”

Fortunately for our Association, this narrow-minded attitude did not prevail, and our records show that while not avoiding controversial and even inflammatory subjects, we have been able to exercise a powerful influence on the progress of science. The establishment of electric units, universally accepted throughout the world, originated in the work of one of our committees; the efforts which led to the foundation of the National Physical Laboratory, one of the most efficient and beneficial organisations in the country, received its first impulses from us, and the organisation of the first world service for the systematic investigation of earth tremors was established by the late Dr. Milne, working through one of our Committees.

The success of these enterprises alone is sufficient to show that we are not merely a body promoting social intercourse between men of science and the rest of the community. Nevertheless, it may be admitted that our efforts have been spasmodic, and the time has arrived to consider whether it may be possible to secure not only a greater continuity in our work but also its better co-ordination with that of other scientific organisations. The present juncture affords the opportunity, and the changed conditions, which in the near future will affect all our institutions, render it indeed incumbent upon us once more to adapt ourselves to the needs of the times. Proposals for a move in that direction have already been made, and will no doubt be carefully considered by the Council. In the meantime, I may draw your attention to the important discussions arranged for by our Economic Section, which alone will justify the decision of the Council not to suspend the meeting this year.

It must not be supposed that, even in the early days of the Association, Whewell's ideas of its functions were universally accepted. It is pleasant to contrast the lamentations of the omniscient Professor of Mineralogy with the weightier opinion of the distinguished mathematician who then held Newton's chair at Cambridge. At the concluding session of the second meeting of the Association, Babbage expressed the hope “that in the selection of the places at which the annual meetings were to be held, attention should be paid to the object of bringing theoretical science in contact with the practical knowledge on which the wealth of the country depends.” “I was myself,” he said, “particularly anxious for this, owing as I do a debt of gratitude for the valuable information which I have received in many of the manufacturing districts, where I have learned to appreciate still more highly than before the value of those speculative pursuits which we follow in our academical labours. I

* Others were allowed to join on recommendation by the General Committee. It was only in 1906 that this restriction, which had become obsolete, was removed.

* It is much to be desired that the documents relating to the early history of the British Association should be published in a collected form.

was one of those who thought at first that we ought to adjourn for our next meeting to some large manufacturing town; but I am now satisfied that the arrangement which has been made will be best adapted to the present state of the Association. When, however, it shall be completely consolidated I trust we may be enabled to cultivate with the commercial interests of the country that close acquaintance which I am confident will be highly advantageous to our more abstract pursuits."

Since then, as we all know, our most successful meetings have been held in manufacturing centres; but it is important to note that, while Babbage laid stress on the benefit which would accrue to pure science by being brought into contact with practical life, scientific men of the present day have more and more insisted on the services they, on their part, are able to render to the industries. The idealistic motive has thus given way to the materialistic purpose. Both aspects are perhaps equally important, but it is necessary to insist, at the present time, that the utilitarian drum can be beaten too loudly. There is more than one point of contact between different activities of the human mind, such as find expression in scientific pursuits or commercial enterprises, and it is wrong to base the advantages to be derived from their mutual influence solely, or even mainly, on the ground of material benefits.

I need not press this point in a city which has given many proofs that a business community may be prompted by higher motives than those which affect their pockets. It was not for utilitarian objects that repeated efforts were made since the year 1640 to establish a University in Manchester; it was not for reasons of material gain that the Royal Institution and Owens College were founded; nor was it because they increased the wealth of the district that the place of honour in our Town Hall has been given to Dalton and Joule.

When we glance at the various occupations of the working parts of a nation, comprising the student who accumulates or extends knowledge, the engineer who applies that knowledge, the geologist or agriculturalist who discloses the store of wealth hidden in the soil, the commercial man who distributes that wealth, it seems as if we ought to be able to name the qualities of intellect and temperament which in each pursuit are most needed to carry out the work successfully. But on trying to define these qualities we soon discover the formidable nature of the task. Reasoning power, inventive power, and sound balance of judgment are essential attributes in all cases, and the problem is reduced to the question whether there are different varieties of the attributes which can be assigned to the different occupations.

Among all subjects mathematics is perhaps the one that appears most definitely to require a special and uncommon faculty. Yet, Poincaré—himself one of the clearest thinkers and most brilliant exponents of the subject—almost failed when he attempted to fix the distinguishing intellectual quality of the mathematician. Starting from the incontrovertible proposition that there is only one kind of correct reasoning, which is logical reasoning, he raises the question why it is that everybody who is capable of reasoning correctly is not also a mathematician, and he is led to the conclusion that the characterising feature is a peculiar type of memory. It is not a better memory, for some mathematicians are very forgetful, and many of them cannot add a column of figures correctly; but it is a memory which fixes the order in which the successive steps of reasoning follow each other without necessarily retaining the details of the individual steps. This Poincaré illustrates by contrasting the memory of a chess-player with that of a mathematician. "When I play chess," he says, "I reason out correctly that if I were to make a certain move, I should expose myself to a certain danger. I should therefore consider a number of other moves, and, after rejecting each of them in turn, I should end by making the one which I first contemplated and dismissed, having forgotten in the meantime the

ground on which I had abandoned it." "Why, then," he continues, "does my memory not fail me in a difficult mathematical reasoning in which the majority of chess-players would be entirely lost? It is because a mathematical demonstration is not a juxtaposition of syllogisms, but consists of syllogisms placed in a certain order, and the order in which its elements are placed is much more important than the elements themselves. If I have this intuition—so to speak—of the order, so as to perceive at once glance the whole of the reasoning, I need not fear to forget its elements: each of these will take its right place of its own accord without making any call on my memory" ("Science et Méthode," pp. 46 and 47).

Poincaré next discusses the nature of the intellectual gift distinguishing those who can enrich knowledge with new and fertile ideas of discovery. Mathematical invention, according to him, does not consist in forming new combinations of known mathematical entities, because the number of combinations one could form are infinite, and most of them would possess no interest whatever. Inventing consists, on the contrary, in excluding useless combinations, and therefore:—"To invent is to select—to choose." . . . "The expression 'choose' perhaps requires qualifying, because it recalls a buyer to whom one offers a large number of samples which he examines before making his choice. In our case the samples would be so numerous that a lifetime would not suffice to complete the examination. This is not the way things are done. The sterile combinations never present themselves to the mind of the inventor, and even those which momentarily enter his consciousness, only to be rejected, partake something of the character of useful combinations. The inventor is therefore to be compared with an examiner who has only to deal with candidates who have already passed a previous test of competence."

All those who have attempted to add something to knowledge must recognise that there is a profound truth in these remarks. New ideas may float across our consciousness, but, selecting the wrong ones for more detailed study, we waste our time fruitlessly. We are bewildered by the multitude of roads which open out before us, and, like Poincaré when he tries to play chess, lose the game because we make the wrong move. Do we not all remember how, after the announcement of a new fact or generalisation, there are always many who claim to have had, and perhaps vaguely expressed, the same idea? They put it down to bad luck that they have not pursued it, but they have failed precisely in what, according to Poincaré, is the essence of inventive power. It may be bad luck not to have had a good idea, but to have had it and failed to appreciate its importance is downright incapacity.

An objection may be raised that before a selection can be made the ideas themselves must appear, and that, even should they arrive in sufficient numbers, the right one may not be among them. It may even be argued that Poincaré gives his case away by saying that "the sterile combinations do not even present themselves to the mind of the inventor, 'putting into a negative form what may be the essence of the matter.'" Moreover, a fertile mind like that of Poincaré would be apt to place too low a value on his own exceptional gifts. Nevertheless, if Poincaré's more detailed exposition be read attentively, and more especially the description of how the discoveries which made him famous among mathematicians originated in his mind, it will be found that his judgment is well considered and should not be lightly set aside. New ideas seldom are born out of nothing. They most frequently are based on analogies, or the recollection of a sequence of thoughts suggested by a different branch of the subject, or perhaps by a different subject altogether. It is here that the memory comes in, which is not a memory of detail, but a memory of premises with their conclusions, detached from the particular case to which they were originally applied. Before we pronounce an adverse opinion on Poincaré's judgment, we must investigate what con-

stitutes novelty in a new idea, but the subject is too vast to be dealt with here, nor can I attempt to discuss whether an essential distinction exists between mathematical invention and that more practical form of invention with which, for instance, the engineer has to deal.

If Poincaré, by this introspective analysis of his own powers, has dimmed the aureole which, in the eyes of the public, surrounds the mathematician's head, he removes it altogether by his definition of mathematics. According to him "mathematics is the art of calling two different things by the same name." It would take me too far were I to try to explain the deep truth expressed in this apparently flippant form: physicists, at any rate, will remember the revolution created in the fundamental outlook of science by the application of the term "energy" to the two quite distinct conceptions involved in its sub-divisions into potential and kinetic energy.

Enough has been said to show that the peculiar powers necessary for the study of one of the most abstract branches of knowledge may be expressed in terms which bring them down to the level at which comparison with other subjects is possible. Applying the same reasoning to other occupations, the same conclusion is inevitable. The commercial man, the politician, and the artist must all possess the type of memory best suited to concentrate in the field of mental vision their own experiences as well as what they have learned from the experience of others, and, further, they must have the power of selecting out of a multitude of possible lines of action the one that leads to success; it is this power which Poincaré calls the inventive faculty.

The argument must not be pushed too far, as it would be absurd to affirm that all differences in the capability of dealing successfully with the peculiar problems that occur in the various professions may be reduced to peculiarities of memory. I do not even wish to assert that Poincaré's conclusions should be accepted without qualification in the special case discussed by him. What is essential, to my mind, is to treat the question seriously, and to dismiss the vague generalities which, by drawing an artificial barrier between different groups of professions, try to cure real or imaginary defects through plausible though quite illusory remedies. All these recommendations are based on the fallacy that special gifts are associated with different occupations. Sometimes we are recommended to hand over the affairs of the nation to men of business; sometimes we are told that salvation can only be found in scientific methods—what is a man of business, and what is a scientific method? If you define a man of business to be one capable of managing large and complicated transactions, the inference becomes self-evident; but if it be asserted that only the specialised training in commercial transactions can develop the requisite faculties, the only proof of the claim that could be valid would be the one that would show that the great majority of successful statesmen, or political leaders, owed their success to their commercial experience. On the other hand, every method that leads to a correct result must be called a scientific method, and what requires substantiating is that scientific training is better than other training for discovering the correct method. This proof, as well as the other, has not been, and I think cannot be, given. When, therefore, one man calls for the conduct of affairs "on business lines" and the other clamours for scientific methods, they either want the same thing or they talk nonsense. The weak point of these assertions contrasting different classes of human efforts is that each class selects its own strongest men for comparison with the weakest on the other side.

The most fatal distinction that can be made is the one which brings men of theory into opposition to men of practice, without regard to the obvious truth that nothing of value is ever done which does not involve both theory and practice. While theory is sometimes overbearing and irritating, there are among those who jeer at it some to whom Disraeli's definition applies: the practical man

is the man who practises the errors of his forefathers. With refined cruelty Nemesis infects us with the disease most nearly akin to that which it pleases us to detect in others. It is the most dogmatic of dogmatics who tirades against dogma, and only the most hopeless of theorists can declare that a thing may be right in theory and wrong in practice.

Why does a theory ever fail, though it may be sound in reasoning? It can only do so because every problem involves a much larger number of conditions than those which the investigator can take into account. He therefore rejects those which he believes to be unessential, and if his judgment is at fault he goes wrong. But the practical man will often fail for the same reason. When not supported by theoretical knowledge he generalises the result of an observation or experiment, applying it to cases where the result is determined by an altogether different set of conditions. To be infallible the theorist would have to take account of an infinite number of circumstances, and his calculations would become unmanageable, while the experimenter would have to perform an infinite number of experiments, and both would only be able to draw correct conclusions after an infinite lapse of time. They have to trust their intuition in selecting what can be omitted with impunity, and if they fail it is mainly due to the same defect of judgment. And so it is in all professions: failure results from the omission of essential considerations which change the venue of the problem.

Though theory and practice can only come into opposition when one of them is at fault, there is undoubtedly a contrast in character and temperament between those who incline more towards the one and those who prefer the other aspect; some like a solitary life at the desk, while others enjoy being brought into contact with their fellows. There have at all times been men predestined by nature to be leaders, and leadership is required in all branches of knowledge, the theoretical as well as the more active pursuits, but we must guard against accepting a man's estimate of his own power to convert his thoughts into acts. In the ordinary affairs of life a man who calls himself a man of action is frequently only one who cannot give any reasons for his actions. To claim that title justly a man must act deliberately, have confidence in his own judgment, sufficient tenacity of purpose to carry it through, and sufficient courage to run the unavoidable risks of possible failure. These risks may be trivial or they may be all-important. They may affect the reputation of one unit of creation or involve the whole life of a nation, and according to the greatness of the issue we shall honour the man who having taken the risks succeeds. But whether the scale be microscopic or interstellar, the essence of the faculty of blending theory and practice is the same, and both men of books and men of action are to be found in the philosopher's study and the laboratory, as well as in the workshop or on the battlefield. Modern science began not at the date of this or that discovery, but on the day that Galileo decided to publish his "Dialogues" in the language of his nation. This was a deliberate act destined to change the whole aspect of science, which, ceasing to be the occupation of a privileged class, became the property of the community. Can you, therefore, deny the claim of being a man of action to Galileo, can you deny it to Pasteur, Kelvin, Lister, and a host of others? There are no doubt philosophers who cannot manage even their own affairs, and whom it would be correct to call pure theorists, but that proves nothing, because their defect makes them worse philosophers as well as worse citizens.

In his Presidential Address, delivered to this Association in 1899, Sir Michael Foster summarised the essential features of the scientific mind. Above all other things he considered that its nature should be such as to vibrate in unison with what it is in search of; further, it must possess alertness, and finally moral courage. Yet after enumerating these qualities he arrives at the same result which I have tried to place before you, that there are no

special peculiarities inherent in the scientific mind, and he expresses this conclusion in the following words:—

"But, I hear some one say, these qualities are not the peculiar attributes of the man of science; they may be recognised as belonging to almost everyone who has commanded or deserved success, whatever may have been his walk in life. That is so. That is exactly what I would desire to insist, that the men of science have no peculiar virtues, no special powers. They are ordinary men, their characters are common, even commonplace. Science, as Huxley said, is organised commonsense, and men of science are common men drilled in the ways of commonsense."

This saying of Huxley's has been repeated so often that one almost wishes it were true, but unfortunately I cannot find a definition of commonsense that fits the phrase. Sometimes the word is used as if it were identical with *uncommon* sense, sometimes as if it were the same thing as common *nonsense*. Often it means untrained intelligence, and in its best aspect it is, I think, that faculty which recognises that the obvious solution of a problem is frequently the right one. When, for instance, I see during a total solar eclipse red flames shooting out from the edge of the sun, the obvious explanation is that these are real phenomena caused by masses of glowing vapours ejected from the sun, and when a learned friend tells me that all this is an optical illusion due to anomalous refraction, I object on the ground that the explanation violates my commonsense. He replies by giving me the reasons which have led him to his conclusions, and though I still believe that I am right I have to meet him with a more substantial reply than an appeal to my own convictions. Against a solid argument commonsense has no power, and must remain a useful but fallible guide which both leads and misleads all classes of the community alike.*

If we must avoid assuming special intellectual qualities when we speak of groups of men within one country, we ought to be doubly careful not to do so without good reason in comparing different nations. So-called national characteristics are in many cases matters of education and training, and if I select one as an example it is because it figures so largely in public discussions at the present moment. I refer to that expedient for combining individual efforts which goes by the name of organisation. An efficient organisation requires a head that directs and a body that obeys; it works mainly through discipline, which is its most essential attribute. Every institution, every factory, every business establishment is a complicated organism, and no country ever came to prominence in any walk of life unless it possessed the ability to provide for the efficient working of such organisms. To say that a nation which has acquired and maintained an empire, and which conducts a large trade in every part of the world, is deficient in organising power is therefore an absurdity. Much of the current self-depreciation in this respect is due to the confusion of what constitutes a true organisation with that modification of it which to a great extent casts aside discipline and substitutes co-operation. Though much may be accomplished by co-operation it is full of danger in an emergency, for it can only work if it be loyally adhered to; otherwise it resembles a six-cylinder motor in which every sparking-plug is allowed to fix its own time of firing. Things go well so long as the plugs agree, but there is nearly always one among them that persists in taking an independent course, and when the machine stops complains that the driver is inefficient. The cry for organisation, justifiable as it no doubt often is, resolves itself, therefore, into a cry for increased discipline, by which I do not mean the discipline enforced at the point of the bayonet, but that accepted by the individual who voluntarily subordinates his personal convictions to the will of a properly constituted authority. This

discipline is not an inborn quality which belongs more to one nation than to another; it is acquired by education and training. In an emergency it is essential to success, but if it be made the guiding principle of a nation's activity it carries dangers with it which are greater than the benefits conferred by the increased facility for advance in some directions.

If there be no fundamental difference in the mental qualifications which lead to success in our different occupations, there is also none in the ideals which move us in childhood, maintain us through the difficulties of our manhood, and give us peace in old age. I am not speaking now of those ideals which may simultaneously incite a whole nation to combined action through religious fervour or ambition of power, but I am speaking of those more individual ideals which make us choose our professions and give us pleasure in the performance of our duties.

Why does a scientific man find satisfaction in studying Nature?

Let me once more quote Poincaré (*loc. cit.*, p. 15):—

"The student does not study Nature because that study is useful, but because it gives him pleasure, and it gives him pleasure because Nature is beautiful; if it were not beautiful it would not be worth knowing, and life would not be worth living. I am not speaking, be it understood, of the beauty of its outward appearance—not that I despise it, far from it, but it has nothing to do with science—I mean that more intimate beauty which depends on the harmony in the order of the component parts of Nature. This is the beauty which a pure intelligence can appreciate, and which gives substance and form to the scintillating impressions that charm our senses. Without this intellectual support the beauty of the fugitive dreams inspired by sensual impressions could only be imperfect, because it would be indecisive and always vanishing. It is this intellectual and self-sufficing beauty, perhaps more than the future welfare of humanity, that impels the scientific man to condemn himself to long and tedious studies. And the same search for the sense of harmony in the world leads us to select the facts which can most suitably enhance it, just as the artist chooses among the features of his model those that make the portrait and give it character and life. There need be no fear that this instinctive and unconscious motive should tempt the man of science away from the truth, for the real world is far more beautiful than any vision of his dreams. The greatest artists that ever lived, the Greeks, constructed a heaven, yet how paltry that heaven is compared to ours! And it is because simplicity and grandeur are beautiful that we select by preference the simplest and grandest facts, and find our highest pleasure, sometimes in following the gigantic orbits of the stars, sometimes in the microscopic study of that minuteness which also is a grandeur, and sometimes in piercing the secrets of geological times which attract us because they are remote. And we see that the cult of the beautiful guides us to the same goal as the study of the useful.

"Whence comes this harmony? Is it that things that appear to us as beautiful are simply those which adapt themselves best to our intelligence, and are therefore the tools which that intelligence handles most easily, or is it all the play of evolution and natural selection? In that case those races only survived whose ideals best conformed with their interests, and while all nations pursued their ideals without regard to consequences, some were led to perdition and others achieved an empire. One is tempted to believe that such has been the course of history, and that the Greeks triumphed over the barbarians, and Europe, inheritor of Greek thought, rules the world because the savages cared only for the sensual enjoyment of garish colours and the blatant noise of the drum, while the Greeks loved the intellectual beauty which is hidden beneath the visible beauty. It is that higher beauty which produces a clear and strong intelligence."

If the mathematician's imagination is fired by the beauty and symmetry of his methods, if the moving spring of his

* Since writing the above, I find on reading Prof. J. A. Thomson's "Introduction to Science" a similar criticism of Huxley's dictum. Prof. Thomson's general conclusions are not, however, in agreement with those here advocated.

action is identical with that of the artist, how much truer is this of the man of science who tries by well-designed experiments to reveal the hidden harmonies of nature? Nor would it be difficult, I think, to trace the gratification inherent in the successful accomplishments of other intellectual pursuits to the same source.

Though Poincaré was, I believe, the first to lay stress on the connection between the search for the beautiful and the achievement of the useful, the æsthetic value of the study of science had previously been pointed out and well illustrated by Karl Pearson in his "Grammar of Science." As expressed by him: "It is this continual gratification of the æsthetic judgment which is one of the chief delights of pure science." Before we advance, however, any special claim for the pursuit of science based on these considerations, we must pause to think whether they do not equally apply to other studies or occupations. For this purpose the nature of the æsthetic enjoyment involved must be remembered. We do not mean by it the pleasure we feel in the mere contemplation of an impressive landscape or natural beauty, but it resembles more the enjoyment experienced on looking at a picture where, apart from the sensual pleasure, we are affected by the relation between the result of the representation and that which is represented. The picture, quite apart from what it may be trying to imitate, has a certain beauty due to its contrast of colours or well-balanced arrangement. We have in one case a number of pigments covering a space of two dimensions, and in the other the natural object in three dimensions, made up of entirely different materials and showing an infinite variety of detail and appearance. By itself alone, either a mere photographic representation or a geometrical arrangement of colour and line leaves most of us cold; though both have their own particular beauty the art consists in bringing them into connection. Bearing in mind the æsthetic value of the relationship of the work of our brain or hand to external facts or appearances, it might easily be shown that what has been said of science equally applies to other studies, such as history or literature. We may even go further, and say that any occupation whatever from which we can derive an intellectual pleasure must possess to a greater or smaller degree the elements of combining the useful with the beautiful.

In order to trace in detail the part played by purely emotional instincts in directing the course of our lives we should have to study the causes which influence a child, free to select his future profession. Having eliminated secondary effects, such as early associations or the personal influence of an inspiring teacher, we should probably be brought to a standstill by the dearth of material at our disposal, or led into error by taking our own individual recollections as typical. Nevertheless it is only through the record of each man's experience that we may hope to arrive at a result. If every man who has reached a certain recognised position in his own subject—it need not be pre-eminence—would write down his own recollections of what led him to make the choice of his profession we might hope to obtain facts on which a useful psychological study might be based. Scientific men as a class are not modest, but they share with other classes the reluctance to speak of their early life, owing to a certain shyness to disclose early ambitions which have not been realised. It requires courage to overcome that shyness, but I think that we need feel no shame in revealing the dreams of our childhood and holding fast to them despite the bondage of our weakness, despite the strife ending so often in defeat, despite all the obstacles which the struggle for existence has placed in our path. In some form they should persist throughout our lives and sustain us in our old age.

But the account of our early life should be simple, detached from any motives of self-depreciation or self-assertion, and free from any desire to push any particular moral or psychological theory. We want to trace the dawn of ambition, the first glimmering in the child's mind

that there is something that he can do better than his fellows, and reminiscences of early likes and dislikes, which, though apparently disconnected from maturer tendencies, may serve as indications of a deep-seated purpose in life. It may be difficult to resist the temptation of trying to justify one's reputation in the eyes of the world, but it is worth making the effort. The only example that I know of such an autobiographical sketch is that of Darwin, which is contained in his "Life and Letters," published by his son, Sir Francis Darwin.

The ambition of a child to be better, cleverer, or more beautiful than its fellows is in the main, I think, a wish to please and to be praised. As the child grows up the ambition becomes more definite. It is not a sordid ambition for ultimate wealth or power, nor is it an altruistic ambition to do good for the sake of doing good. Occasionally it takes the form confessed to by Darwin when he says, "As a child I was much given to inventing deliberate falsehoods, and this was always done for the sake of causing excitement." This desire to be conspicuous was in Darwin's case consistent with extreme modesty, amounting almost to a want of confidence in himself, as appears in this passage: "I remember one of my sporting friends, Turner, who saw me at work with my beetles, saying that I should some day be a Fellow of the Royal Society, and this notion seemed to me to be preposterous."

We next come to the stage where a child is attracted by one subject more than another, and if his choice be free will select it for his life's career. What guides him in this choice? If it be said that a boy gravitates towards that subject which he finds easiest, we are led to the further question, why does he find it easiest? It is on this point that more information is required, but I am inclined to answer in accordance with Poincaré's views, that it is because its particular beauty appeals most strongly to his emotional senses. In questions of this kind everyone must form his own conclusions according to his personal recollections, and these convince me that the emotional factor appears already at an early age. It is the strong attraction towards particular forms of reasoning, more perhaps even than the facility with which reasoning comes, that carries us over the initial difficulties and the drudgery that must accompany every serious study.

I have already alluded to the different tendencies of individuals either to prefer solitary reflection or to seek companionship. Almost in every profession we find men of both types. Darwin's autobiography furnishes a good example of the man who prefers to learn through quiet reading rather than through lectures, but to many men of science the spoken word is inspiring and contact with congenial minds almost a necessity.

From our present point of view the most interesting passages in Darwin's autobiography are those indicating the æsthetic feeling which, like Poincaré, he connects with scientific research. Referring to his early studies we find this passage:—"I was taught by a private tutor, and I distinctly remember the intense satisfaction which the clear geometrical proofs gave me. I remember with equal distinctness the delight which my uncle gave me by explaining the principle of the vernier of a barometer." To a man who apparently had no pronounced facility of mastering mathematical difficulties this feeling of satisfaction is especially remarkable. The combination of scientific ability with leanings either to music or art or poetry is very common, and examples are to be found in almost every biography of men of science. It is difficult indeed to name an eminent scientific man who has not strong leanings towards some artistic recreation. We find the poetic vein in Maxwell and Sylvester, the musical talent in Helmholtz and Rayleigh, and the enthusiastic though amateurish pictorial efforts of less important men. That the similarities are to be found also in temperament may be noticed on reading Arnold Bennett's article on "The Artist and the Public" (*English Review*, October, 1913), where many passages will be seen to be applicable to students of science as well as to writers of fiction.

If we look for distinctions between different individuals we may find one in their leanings either towards the larger aspects of a question or the microscopic study of detail. The power of focussing simultaneously the wider view and the minute observation is perhaps the most characteristic attribute of those who reach the highest eminence in any profession, but the great majority of men have a notable predilection for the one or other side. Though it is indispensable for a scientific man to study the details of the particular problem he is trying to solve, there are many who will lose interest in it as soon as they believe they can see a clear way through the difficulties without following up their solution to its utmost limits. To them detail, as such, has no interest, and they will open and shut a door a hundred times a day without being even tempted to inquire into the inner working of the lock and latch.

There is only one feature in the operation of the intelligence by means of which a sharp division may possibly be drawn between brain-workers showing special capabilities in different subjects. In some persons thought attaches itself mainly to language, in others to visualised images, and herein lies perhaps the distinction between the literary and scientific gift. Those who, owing to external circumstances, have resided in different countries are sometimes asked in what language they think. Speaking for myself, I have always been obliged to answer that, so far as I can tell, thought is not connected with any language at all. The planning of an experiment, or even the critical examination of a theory, is to me entirely a matter of mental imagery, and hence the experience, which I think many scientific men must have shared, that the conversion of thought into language, which is necessary when we wish to communicate its results to others, presents not only the ordinary difficulties of translation but reveals faults in the perfection or sequence of the images. Only when the logic of words finally coincides with the logic of images do we attain that feeling of confidence which makes us certain that our results are correct.

A more detailed examination of the instinctive predilections of a child would, I think, confirm Poincaré's conclusion that a decided preference for one subject is in the main due to an unconscious appeal to his emotions. It should be remembered, however, that the second step in Poincaré's philosophy is as important as the first. The mere emotional impulse would die out quickly, if it were not supplemented by the gratification experienced on discovering that the search for the beautiful leads us to results which satisfy our intellect as well as our emotions. There may still be bifurcations in the second portion of the road. Some may rest content with achieving something that supplies the material needs of humanity, others may be inspired to search for the deeper meaning of our existence.

There remains therefore some justification for the question why we persist in studying science apart from the mere intellectual pleasure it gives us. It was once a popular fallacy to assume that the laws of Nature constituted an explanation of the phenomena to which they applied, and people then attached importance to the belief that we could gauge the mind of the Creator by means of the laws which govern the material world, just as we might trace the purpose of a human legislator in an Act of Parliament. As this archaic interpretation was abandoned philosophers went, in accordance with what politicians call the swing of the pendulum, to the other extreme. We can explain nothing, they said; in fact we can know nothing; all we can do is to record facts. This modesty was impressive and it became popular. I know, at any rate, one scientific man who has acquired a great reputation for wisdom by repeating sufficiently often that he knows nothing, and though his judgment may be true this frame of mind is not inspiring. As a corrective

the older visionary claims, which centred round the meaning of the word "explain," the view that the first task of science is to record facts has no doubt had a good

influence. Kirchhoff laid it down definitely that the object of science is to describe nature, but he did not thereby mean that it should be confined to recording detached observations: this would be the dulllest and most unscientific procedure. Description, in the sense in which Kirchhoff uses it, consists in forming a comprehensive statement gathering together what till then was only a disconnected jumble of facts. Thus the apparently quite irregular motions of the planets as observed from the earth were first collected in tabular form. This was a necessary preliminary but was not in itself a scientific investigation. Next came Kepler, who by means of three laws summed up the facts in their main outlines, and the description then took a more refined form, substituting half a page of printing for volumes of observations. Finally Newton succeeded in predicting the planetary movements on the assumption of a gravitational attraction between all elements of matter. According to Kirchhoff the chief merit of this discovery would lie in its condensing Kepler's three laws into one hypothesis. This point of view is not necessarily opposed to that of Poincaré, because it is exactly the simplicity of Newton's explanations that appeals most strongly to our æsthetic sense, but there is an important difference in the manner of expression. However beautiful an idea may be, it loses its effect by being placed before us in an unattractive form. This criticism also applies to Mach, according to whom the object of science is to economise thought, just as it is the object of a machine to economise effort. Logically this definition is justified, and it may be the best that can be given, if we prefer using a technical expression to confessing an emotional feeling. But why should we do so? Is it not better to recognise that human intelligence is affected by sentiment as much as by reasoning? It is a mistake for scientific men to dissociate themselves from the rest of humanity by placing their motives on a different and at the best only superficially higher level. When an adventurous spirit, for instance, desires to organise an expedition to unknown regions of the world we try to induce our Governments to provide the necessary funds by persuading them, and incidentally ourselves, that we do so because important scientific results may be expected from the expedition. This may actually be the case, but we are mainly affected by the same motives as the rest of the community. If the truth be told we are as curious as they to know what every corner of the earth looks like, and we join them in wishing to encourage an enterprise requiring perseverance and involving danger.

I fully realise that the wish to justify one's own work in the eyes of the world will always lead to fresh attempts to find a formula expressing the objects which we desire to attain. Enough, however, has been said to show that the definition must take account of sentiment, without insisting too much upon it. Nor can we hope, in view of the variety of intellectual and emotional pleasures which combine to create the charm of science, to include all points of view, but if I were forced to make a choice I should say that the object of science is to predict the future. The wish to know what lies before us is one of the oldest and most enduring desires of human nature; often, no doubt, it has degenerated and given rise to perverted and ignoble longings, but its accomplishment, when it can be achieved by legitimate inquiry, is a source of the purest and most satisfying enjoyment that science can give. We feel that enjoyment each time we repeat an old and perhaps hackneyed experiment. The result is known beforehand, but be it only that we expect the colour of a chemical precipitate to be green or yellow, be it only that we expect a spot of light to move to the right or left, there is always a little tremor of excitement at the critical moment and a satisfying feeling of pleasure when our expectation has been realised. That pleasure is, I think, enhanced when the experiment is not of our own making but takes place uncontrolled by human power. In one of Heine's little verses he makes light of the tears of a young lady who is moved by the setting sun. "Be of good

cheer," the poet consoles her, "this is only the ordinary succession of events: the sun sets in the evening and rises in the morning." If Heine had been a man of science, he would have known that the lady's tears found a higher justification in the thought of the immutable and inexorable regularity of the sun's rising and setting than in the fugitive colour impression of his descent below the horizon, and that her emotions ought to be intensified rather than allayed by the thought of his resurrection in the morning—everybody's life contains a few unforgettable moments which, at quite unexpected times, will vividly rise in his mind, and there are probably some in this Hall who have experienced such moments at the beginning of a total eclipse of the sun. They have probably travelled far, and gone through months of preparation, for an event which only lasts a few minutes. The time of first contact is approaching, in a few seconds the moon is about to make its first incision in the solar disc, and now the observer's thoughts come crowding together. What if there were a mistake in our calculations? What if we had chosen a spot a few miles too far north or too far south? What if the laws of gravitation were ever so little at fault?—But now at the predicted time, at the calculated spot on the sun's edge, the dark moon becomes visible, and the feeling of relief experienced concentrates into one tense instant all the gratitude we owe those who have given precision to the predictions of celestial movements, leaving them expressible by a simple law which can be written down in two lines. It is this simplicity of the law of gravitation, and its accuracy, which some day may show limitations, but has hitherto withstood all tests, that gives to Astronomy its pre-eminence over all sciences.

Indeed, if we classify the different sections into which science may be divided, I think it may be said that their aim, in so far as it is not purely utilitarian, is always either historic or prophetic, and to the mathematician, history is only prophecy pursued in the negative direction. It is no argument against my definition of the objects of science, that a large section of its sub-divisions has been, and to some extent still is, mainly occupied with the discovery and classification of facts; because such classification can only be a first step, preparing the way for a correlation into which the element of time must enter, and which therefore ultimately must depend either on history or prophecy.

Lastly, men of science, and in particular physicists, have given increased attention to the intrinsic meaning of the concepts by means of which we express the facts of Nature. Everything—who can deny it?—is ultimately reduced to sense impressions, and it has therefore been asserted that science is the study of the mind rather than of the outside world, the very existence of which may be denied. The physicist has thus invaded the realm of philosophy and metaphysics, and even claims that kingdom as his own. Two effects of these efforts, a paralysing pessimism and an obscure vagueness of expression, if not of thought, seriously threatened a few years ago to retard the healthy progress of the study of Nature. If the outside world were only a dream, if we never could know what really lies behind it, the incentive which has moved those whose names stand out as landmarks in science is destroyed, and it is replaced by what? By a formula which only appeals to a few spirits entirely detached from the world in which they live. Metaphysicians and physicists will continue to look upon science from different points of view, and need not resent mutual criticisms of each other's methods or conclusions. For we must remember that most of the good that is done in this world is done by meddling with other people's affairs, and though the interference is always irritating and frequently futile, it proves after all that our interests converge towards a common centre.

According to Poincaré, the pleasure which the study of science confers consists in its power of uniting the beautiful with the useful; but it would be wrong to adopt this formula as a definition of the object of science, because it applies with equal force to all human studies. I go

further, and say that the combination of the search for the beautiful with the achievement of the useful is the common interest of science and humanity. Some of us may tend more in one direction, some in another, but there must always remain a feeling of imperfection and only partial satisfaction unless we can unite the two fundamental desires of human nature.

I have warned you at the beginning of this discourse not to beat the utilitarian drum too loudly, and I have laid stress throughout on the idealistic side, though the most compelling events of the moment seem to drive us in the other direction, and the near future will press the needs of material prosperity strongly upon us. I must guard myself, therefore, against one criticism which the trend of my remarks may invite. At times, when the struggle for existence keeps masses in permanent bondage, in a society in which a multitude of men and women have to face starvation, and when unfortunate, though purely accidental, surroundings in childhood drive the weak into misery, is it not futile to speak of æsthetic motives? Am I not, while endeavouring to find a common bond between all sections of the community, in reality drawing a ring round a small and privileged leisured class, telling them these enjoyments are for you and for you alone? Should I not have found a surer ground for the claims of science in its daily increasing necessity for the success of our manufactures and commerce?

I have said nothing to indicate that I do not put the highest value on this important function of science, which finds its noblest task in surrendering the richness of its achievements to the use of humanity. But I must ask you to reflect whether the achievement of wealth and power, to the exclusion of higher aims, can lead to more than a superficial prosperity which passes away, because it carries the virus of its own doom within it. Do we not find in the worship of material success the seed of the pernicious ambition which has maddened a nation, and plunged Europe into war? Is this contempt for all idealistic purposes not responsible for the mischievous doctrine that the power to possess confers the right to possess, and that possession is desirable in itself without regard to the use which is made of it? I must therefore insist that if we delight in enlisting the wealth accumulated in the earth, and all the power stored in the orbs of heaven, or in the orbits of atomic structure, it should not be because we place material wealth above intellectual enjoyment, but rather because we experience a double pleasure if the efforts of the mind contribute to the welfare of the nation. When Joule taught us to utilise the powers at our disposal to the best advantage he did it not—and his whole life is a proof of it—to increase either his own wealth or that of the nation, but because, brought up in commercial life and deeply imbued with the deep insight and genius of science, he found his greatest delight in that very combination of æsthetic satisfaction and useful achievement which Poincaré has so well described. And, again, when another of our fellow-citizens, Henry Wilde, showed how electrical power can be accumulated until it became an efficient instrument for the economic transmission of work, he found his inspiration in the intellectual gratification it gave him, rather than in the expectation of material gain. I am drawing no ring round a privileged class, but urge that the hunger for intellectual enjoyment is universal, and everybody should be given the opportunity and leisure of appeasing it. The duty to work, the right to live, and the leisure to think are the three prime necessities of our existence, and when one of them fails we only live an incomplete life.

I should have no difficulty in illustrating by examples, drawn from personal experience, the power which the revelations of science can exert over a community steeped in the petty conflicts of ordinary life; but I must bring these remarks to a conclusion, and content myself with the account of one incident.

An American friend, who possessed a powerful telescope, one night received the visit of an ardent politician. It was

the time of a Presidential election, Bryan and Taft being the opposing candidates, and feeling ran high. After looking at clusters of stars and other celestial objects, and having received answers to his various questions the visitor turned to my friend:—

"And all these stars I see," he asked, what space in the heaven do they occupy?"

"About the area of the moon."

"And you tell me that every one of them is a sun like our own?"

"Yes."

"And that each of them may have a number of planets circulating round them like our sun?"

"Yes."

"And that there may be life on each of these planets?"

"We cannot tell that, but it is quite possible that there may be life on many of them."

And after pondering for some time, the politician rose and said:—"It does not matter after all whether Taft or Bryan gets in."

Happy were the times when it could be said with truth that the strife of politics counted as nothing before the silent display of the heavens. Mightier issues are at stake to-day; in the struggle which convulses the world, all intellectual pursuits are vitally affected, and Science gladly gives all the power she wields to the service of the State. Sorrowfully she covers her face because that power, accumulated through the peaceful efforts of the sons of all nations, was never meant for death and destruction; gladly she helps, because a war wantonly provoked threatens civilisation, and only through victory shall we achieve a peace in which once more Science can hold up her head, proud of her strength to preserve the intellectual freedom which is worth more than material prosperity, to defeat the spirit of evil that destroyed the sense of brotherhood among nations, and to spread the love of truth.

THE ANALYSIS OF PLATINUM.*

By F. MYLIUS and A. MAZZUCHELLI.

(Continued from p. 126).

III. QUANTITATIVE ANALYSIS OF IMPURE PLATINUM.

The method of qualitative analysis just described cannot be directly applied to the quantitative analysis of alloys rich in platinum, because at various stages mixed "waste products" are present, which hinder the complete separation.

It is much easier if no attention need to be paid to the presence of ruthenium, as is the case with technical platinum metal. This contains at most only traces of ruthenium, which can be neglected in an approximate analysis.

The determination of foreign metals is rendered more difficult by a large excess of platinum, which makes a change of the whole process *a priori* necessary. This consists in first separating the excess of platinum so that (as in the case described) the other constituents may be present in about the right amount for analysis. From a practical point of view two cases are to be distinguished.

Case A.—The platinum metal is so impure that the other constituents can first be separated by a summary precipitation previous to a closer investigation.

Case B.—The platinum is so pure that the direct precipitation of the other constituents is not possible. In this case the platinum must first be separated as sodium platinum chloride from alkaline solution (*cf.*, *prox.*). The small impurities are then sought for in the mother liquor.

Preliminary Examination.

To determine whether a platinum material is to be treated according to case A or case B, a preliminary ex-

amination "for purity" must be performed with 0.1 grm. of metal, as in the test for iridium. The solution in aqua regia is evaporated to dryness with 0.1 grm. of sodium chloride, the residue is dissolved in 10 cc. of water, and warmed to 100° in a test-tube with a little soda (about 0.02 grm.), so that litmus-paper is coloured faintly blue. After cooling, 1–2 drops of sodium hypochlorite or hypobromite solution are added and the solution is again warmed. If the solution keeps its orange-yellow coloration without giving any precipitate nominally pure platinum is present (case B), but if a dark coloration appears which settles to a blue-black precipitate, the presence of other constituents is indicated, and the platinum under examination is an impure or technical platinum (case A).

The further examination of this reaction has shown that it allows of the almost complete separation as oxides of all the other impurities to be taken into account as well as iridium. Thus only a very small amount remains in the filtrate, which is rich in platinum. Even gold which of itself is not precipitated goes over almost entirely into the precipitate. (*Note.*—The traces of gold still remaining in the solution may be precipitated if the filtrate containing hypobromite is warmed with some alcohol; any other traces of impurities still present—*e.g.* ruthenium—besides a little platinum are also separated thus).

This precipitation method is also suitable for employment in the quantitative analysis of impure platinum, for it provides a convenient means of separating all impurities from platinum. The method recalls the preparatory purification process of v. Schneider (*Lieb. Ann. v. Suppl.*, 1867, 261, *cf.* Muspratt, v., 291), in which the red platinum solution is boiled with caustic soda. But this process effects a reduction according to the original aim, and the iridium mostly remains in solution as trichloride. (Still more if it is boiled with milk of lime according to Doebereiner's method). Our hypochlorite method, on the contrary, is an oxidation process, and separates the iridium with the other foreign metals as oxide.

Platinum Ore.—The applicability of the following process for the quantitative analysis of technical platinum would be particularly obvious if it could be employed for the analysis of natural platinum ore which contains an unequally large amount of other constituents. We have therefore laid stress upon obtaining an estimate of the value of our method by the repeated analysis of granular platinum ore (obtained from Heraeus), but we only investigated the part of the ore which is soluble in aqua regia. The composition is given later on. Besides the following ten metals which can be determined—Pt, Ir, Rh, Pd, Au, Ag, Cu, Fe, Ni, Co—traces of other impurities may be present which escaped us owing to their insignificant quantity. For the proximate analysis it is convenient to use a grm. The separation of the constituents by alkaline hypochlorite solution is easy and occurs almost of itself, so that the traces remaining in the solution may be neglected. In spite of its great volume (mostly caused by the presence of iron) the precipitate contains only about 1 per cent of all the platinum; this quantity can be precipitated directly from the filtrate by hydrazine hydrochloride and determined in sufficient purity by igniting; the solution of its chloride gave a light yellow precipitate with ammonium chloride. The separation of the other constituents occurs with the desired regularity, and the excess of iron produces no ill effects.

The nickel and cobalt which have been proved to be present in natural platinum ore make it necessary to take these metals also into account in the analysis of technical platinum.

Quantity for Analysis.—As the difficulty of isolating in a pure state the individual constituents of an impure platinum metal increases as the mass decreases, the possibility of applying a method of proximate analysis depends very much upon the amount of material at one's disposal.

While it is generally possible to detect any secondary constituents by using a decigram of platinum metal, a grm.

* *Zeitschrift für Analytische Chemie*, lxxxix., 1.

of it enables the relative amounts of the individual impurities to be established with more certainty.

The use of 10 grms. of technical platinum is to be recommended, when the following method is to be used for an approximate analysis, which is sufficient for most purposes. A maximum error of ± 10 per cent is allowable in it in the small impurities (of 0.1 to 0.2 per cent). (Larger quantities of material are necessary for the accurate determinations).

But if it is a question of a trustworthy analytical examination of nominally "pure platinum" (case B), as much as 100 grms. of the metal must be used according to the requirements. The task is then the same as the proof of the degree of purity of any common heavy metal (copper, lead, zinc, tin, nickel, &c.), which can only be done successfully with large quantities (*cf.* Mylius, *Zeit. Anorg. Chem.*, 1912, xlvii., 407).

While in the analysis of specially prepared platinum alloys usually the determination of the platinum is the object, the amount of it in the cases described here is determined indirectly from the sum of the other constituents; the direct determination of the platinum would be as tedious as it is useless.

(To be continued.)

THE VAPOUR PRESSURE OF CONCENTRATED SUGAR SOLUTIONS.*

By D. ORSON WOOD, B.Sc., A.R.C.Sc.

(Continued from p. 103).

Von Babo's Law and the Theory of Solution.—Babo showed that, for dilute solutions, the lowering of the vapour pressure relative to that of the solvent ($\frac{\pi_0 - \pi_\pi}{\pi_0}$) was independent of the temperature for the same solution, and theory (*e.g.*, Kirchhoff's equation) has since proved that this will only be true when the latent heat of dilution is zero. The values of this ratio calculated from the present observations are shown in Tables IV. and VI., and while the variation is far smaller than that obtained by Perman and Price, yet, as the calculation of the latent heat of dilution shows, it is seemingly still too large.

It is usual to calculate the molecular weight of the solute in solution from the expression—

$$M = \frac{\pi_\pi}{\pi_0 - \pi_\pi} \times \frac{18w}{W},$$

where w grms. of solute are dissolved in W grms. of solvent. If this is applied to the present case, the values of M obtained for Solutions I., II., and III. at 75° C. are 303, 230, and 175 respectively, thus decreasing with increase of concentration, and for II. and III. increasing with rise of temperature. Inasmuch as this equation is based on the simple form of Raoult's law (that

$$\frac{\pi_0 - \pi_\pi}{\pi_0} = \frac{n}{N},$$

where n gm. molecules of solute are dissolved in N of solvent), which most certainly is not true here, the calculation has no real meaning.

Callendar (*Proc. Roy. Soc.*, A, 1908, 90) has elaborated the vapour pressure theory due to Poynting, and, according to his view, when the heat of dilution is small, as it is, at any rate with moderately strong sugar solutions—

$$\pi_\pi = \frac{N - an}{N - an + n} \pi_0,$$

where a is a hydration factor representing the number of solvent molecules associated with each molecule of solute. From experiments on the osmotic pressure of sugar solu-

tions at room temperatures and also on the lowering of freezing-point, with solutions of concentration up to 7 molecules of sugar to 100 of water, Callendar found that $a=5$; though the value showed signs of falling off with the greatest concentration. The values of a calculated from my values of the vapour pressure π_π are shown in Table VI.

It will be seen that a does not vary greatly either with concentration or temperature, but is decidedly less than 5. In fact the mean value for Solution II. is 3.97 and for III. 4.13; that is, 4 in each case, within the limits of experimental error. The calculations are based on values of π_0 taken from Kaye and Laby's tables. If my values are used instead, a is less, but does not undergo any important alteration. It seemed best to use the standard values of π_0 , since the cause of mine being too low is uncertain. The values of π_π required to make $a=5$ have been calculated in each case, and, as will be seen from the table, they are much smaller than those observed. They are quite out of the range of the experimental error indicated by the experiment with pure water, which gave values too low and not too high, as these would need to be to make a greater. Assuming, however, that the difference is due to experimental error, it might arise in two ways:—

(i.). Air not sufficiently removed from the solution. No less care was taken to remove the air from the solutions than with the water; moreover, it is suggestive that the supposed error in π_π increases with rise of concentration (at 90° C. the difference is 0.20, 0.91, and 3.21 for Solutions I. II., and III. respectively), and does not vary in a random fashion, as might be expected, from a fortuitous quantity of residual air. As a matter of fact, it was feared that Experiment II. might fail owing to leakage through the glass of the filler tube, which had devitrified with frequent fusing at the cut E (Fig. 1).

TABLE VI.

Temp.	π_0	π_π	$\pi_0 - \pi_\pi$	$\frac{\pi_0 - \pi_\pi}{\pi_0}$	a	π_π (calc.) $a=5$	$\pi_\pi - \pi_\pi$ $a=5$
Solution II. $n/N = 0.0824$.							
60°	14.92	13.19	1.73	0.116	4.51	13.09	0.10
65°	18.75	16.68	2.07	0.110	4.04	16.44	0.24
70°	23.34	20.84	2.50	0.107	3.78	20.46	0.38
75°	28.92	25.75	3.17	0.110	4.04	25.37	0.38
80°	35.52	31.68	3.84	0.108	3.85	31.17	0.51
85°	43.31	38.72	4.59	0.106	3.69	37.99	0.73
90°	52.55	47.06	5.49	0.105	3.60	46.15	0.91
Solution III. $n/N = 0.1182$.							
60°	14.92	11.87	3.05	0.204	4.56	11.58	0.29
65°	18.75	15.02	3.73	0.199	4.43	14.53	0.49
70°	23.34	18.79	4.55	0.195	4.33	18.09	0.70
75°	28.92	23.40	5.52	0.191	4.22	22.40	1.00
80°	35.52	29.16	6.36	0.179	3.87	27.54	1.62
85°	43.31	35.80	7.51	0.174	3.71	33.60	2.20
90°	52.55	43.28	9.27	0.176	3.78	40.07	3.21

(ii.). Concentrations incorrect. Taking the average values of $\frac{\pi_0 - \pi_\pi}{\pi_0}$, a would become 5 if the concentrations (n/N) were 0.0435, 0.0758, and 0.1073 instead of 0.0824, 0.0824, and 0.1182 respectively. Thus the solutions would need to be weaker than they were estimated to be, while in reality, as has been pointed out already, the calculated value must be, if anything, too small. The differences, then, are real, and it remains to inquire what may be taking place in the solution in order to account for them.

The relation from which a is calculated is only intended to apply when the latent heat of dilution is small. This may be seen at once by writing it in the form—

$$a = \frac{N+n}{n} - \frac{1}{\frac{\pi_0 - \pi_\pi}{\pi_0}}$$

* A Paper read before the Faraday Society, May 11, 1915.

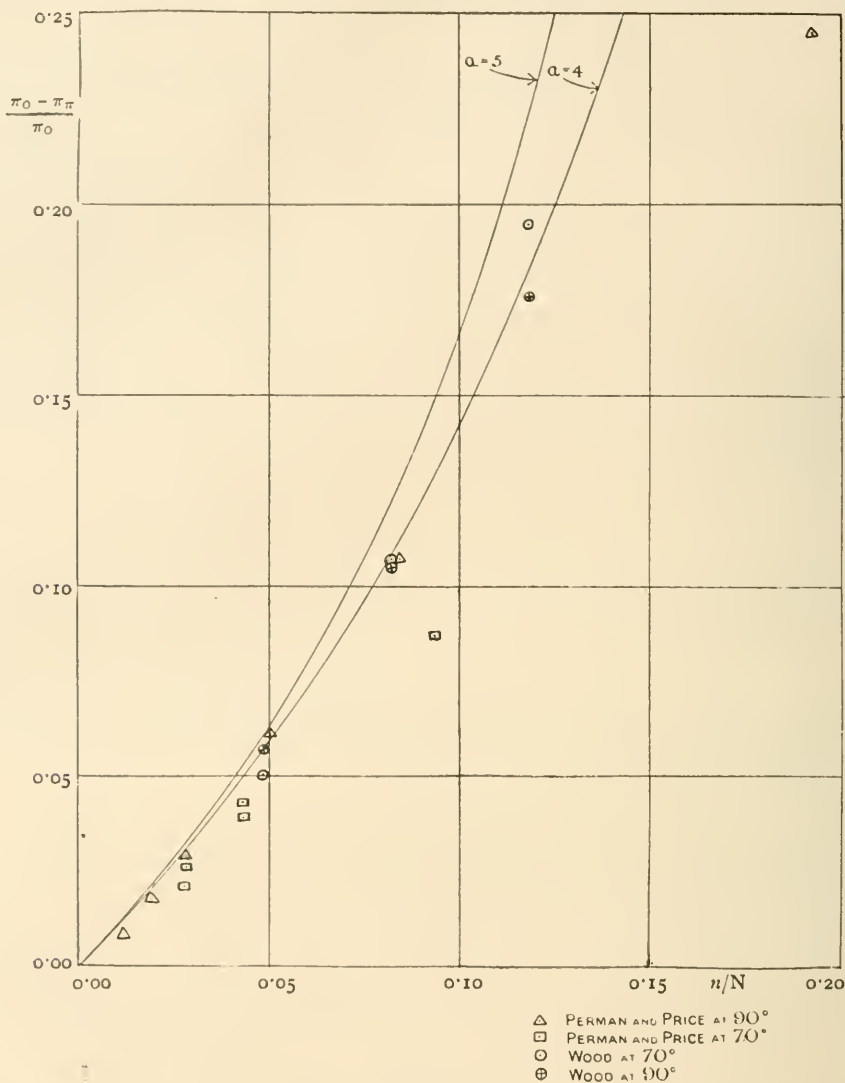


FIG. 3.

For a solution of given strength $\frac{N+n}{n}$ is constant.

Therefore the constancy of a would imply the constancy of $\frac{\pi_0 - \pi_\pi}{\pi_0}$, which is an approximate form of $\log_e \frac{\pi_0}{\pi_\pi}$, and this, according to Kirchhoff, is constant only when H , the dilution heat, is zero. If H is not zero the relation may perhaps still be used by writing n' for n , where n' represents the effective number of sugar molecules present in N of water, calculated so as to keep a constant (Callendar, *loc. cit.*). This change is equivalent to that made to allow for the ionisation of electrolytes, and, since the heat of dilution is generally connected with association or dissociation of molecules, the alteration is not unreasonable.

The values of n' , assuming $a=5$, are shown in Table VII. below for solution III., for which n is 11.82 molecules per 100 of water.

TABLE VII.

Temperature.	60°.	70°.	80°.	90°.
n'	11.23	10.95	10.43	10.33

It will be seen that the effective number of solute molecules calculated in this way decreases as the temperature rises, thus implying association of the solute increasing with rise of temperature. This result will always be obtained when the latent heat of dilution is negative, for then $\frac{\pi_0 - \pi_\pi}{\pi_0}$ must decrease with rise of temperature; consequently so must

$$\frac{n'}{N - (a-1)n'} \quad \text{or} \quad \frac{n'}{N - 4n'}$$

in the present case when a is constant and = 5. This requires that n' itself should diminish, N of course being constant. It seemed at first sight as if this result was contrary to the laws of thermodynamics, but such is not the case. The van't Hoff isochor leads to the well known statement that "rise of temperature favours the system formed with absorption of heat." Therefore an association which increases with rise of temperature must be endothermic. Now, dilution of constant temperature causes the associated molecules to dissociate again, since for weak solutions $n'=n$, i.e., it produces an exothermic reaction, so that the latent heat of dilution is negative.

If this association does not occur, then the only alternative is to suppose that lower hydrates are formed, and that there are present in a given solution at a given temperature definite proportions of two or more different hydrates. The observations are neither sufficiently numerous nor sufficiently accurate to indicate the law governing the variation of this hydration with concentration, only the change is probably very small.

Thus far the discussion has been limited to the variation of vapour pressure with temperature at constant mass concentration. There is very little to be said about the variation of pressure with concentration. Fig. 3 is drawn to show the manner in which the ratio $\frac{p_p - p_0}{p_p}$ varies at 70° and 90° C. The diagram shows (a) Perman and Price's measurements, (b) the results recorded in this paper, and (c) curves calculated from Callendar's formula by putting $a=4$ and 5. It will be seen that Perman's values lie on straight lines, specially those at 90° C., implying that Wüllner's law is obeyed, but some little adjustment would be necessary to make the points pass through the origin. The experimental values appear to correspond well with Callendar's curve when $a=4$ not 5, but it must be remembered that the curves obtained by giving a successive integral values are quite close together, and this is more particularly the case when n/N is small; thus my two points at 70° and 90° C. for $n/N=0.0486$ correspond to $a=1.66$ and $a=3.97$ respectively.

According to Perman's observations the vapour pressure is inversely proportional to the concentration n/N , while my measurements indicate that it decreases more rapidly than this.

(To be continued).

NOTICES OF BOOKS.

Aids to the Analysis and Assay of Ores, Metals, Fuels, &c.
By J. JAMES MORGAN, F.I.C., F.C.S. Second Edition.
London: Ballière, Tindall, and Cox. 1915.

THIS book, which has undergone very little change in its second edition beyond revision and the addition of some supplementary matter, contains concise directions for the analysis and assay of the more important ores and metals, fuels, &c. As a rule no choice of methods is given, and only those are described which the experience of the author and others has shown to be trustworthy and satisfactory from every point of view. Liquid fuels are included, but no details are given of Abel's standard apparatus for flash-point determinations. Simple gas analysis, and the examination of fireclay, fuel ash, boiler incrustations, water, &c., are described, and the book can be recommended as a useful introduction to technical analysis, suitable for students who have had some experience in analytical work.

Gas Engineering and Gas Manufacture. A Review of the Institution of Gas Engineers. Edited by CHARLES W. HASTINGS. London: J. G. Hammond and Co., Ltd. 1915.

THIS volume, which will be of considerable permanent value as a record of progress in gas manufacture, contains a short review of the Transactions of the Institution of Gas Engineers. The presidential addresses, and the important papers read at the meetings are abstracted, and the reports prepared by the Research Committees and read before the Institution are also briefly noticed. The whole gives a clear summary of the growth of the industry, and as the author was present at nearly every meeting since 1877 and knew personally every president, he has been able to intersperse many personal and biographical notes and interesting comments.

Prospectus of University Courses in the Municipal School of Technology, Manchester, 1915-16.

THIS prospectus contains descriptions of the excellent equipment of the Manchester Municipal School of Technology, and its work and aims are discussed. Full information is given about the laboratories and useful summaries of the approved courses of work are provided. These summaries show that the foundations of a wide and liberal technical education can be laid at the school, whose students should be well equipped for their life-work and imbued with a thoroughly scientific spirit of openmindedness and research.

Elementary Chemical Microscopy. By EMILE MOUNIN CHAMOT, B.S., Ph.D. New York: John Wiley and Sons, Inc. London: Chapman and Hall, Ltd. 1915.

ACCORDING to the author of this treatise American chemists have been comparatively neglectful of chemical microscopy, partly owing to the lack of elementary books on the subject, which has resulted in a lack of skill and knowledge on the part of workers in chemical laboratories. To remedy this want he has compiled a useful book. The apparatus described in it is that in use at Cornell University and has been thoroughly tested. The student who uses the book is supposed to have studied crystallography and optics, but brief notes are given on the construction and use of various instruments, so that he may refresh his memory upon forgotten points. The ultramicroscope is described in full, with clear illustrations and details of useful accessories, such as mechanical stages, object slides, work tables, &c. Work with polarised light, the examination of crystals, and the determination of refractive indices are treated in subsequent chapters, and the use of the microscope for quantitative analysis, especially in food analysis, is well explained. Directions are then given for using reagents in microchemical qualitative analysis, and the student is advised to make himself thoroughly proficient in experimental work of this nature before he proceeds to the examination of the microchemical reactions of the common elements and acids in simple mixtures described in the last chapter.

The Examination of Hydrocarbon Oils and of Saponifiable Fats and Waxes. By Prof. Dr. D. HOLDE. Authorised Translation from the fourth German Edition by EDWARD MUELLER, Ph.D. New York: John Wiley and Sons, Inc. London: Chapman and Hall, Ltd. 1915.

THIS book is characterised by the completeness with which it treats of the hydrocarbon oils, and English-speaking chemists will no doubt readily appreciate its value as a reference book in their laboratory investigations. The examination of petroleum and petroleum products, lubricants, asphalt, tars, waxes, saponifiable fats and technical products obtained from them is included, and by judicious condensation and selection of material a very large amount of information is compressed into the book.

The Smelting of Copper Ores in the Electric Furnace. By DORSEY A. LYON and ROBERT M. KEENEY. Washington: Government Printing Office. 1915.

THIS bulletin contains a critical discussion of the possibility of smelting copper ores in the electric furnace, and gives the results of the experimental work of the authors and other investigators on the electric smelting of copper. The electric furnace is compared with the blast and reverberatory furnaces, and the authors show that it may with advantage be used in certain localities to replace them, as, for example, if the cost of coke for smelting is very high, or if electric power can be obtained at a comparatively low cost owing to the fact that water-power is at hand. The chemistry of copper smelting is very briefly summarised, and then the authors' experiments on the

feasibility of smelting fine Michigan native copper concentrates are described in detail, and the process which could be based upon them is explained. The smelting of sulphide copper ores is then treated and the work of various investigators is discussed. Some of the general conclusions the authors draw are:—1. Native copper, oxide, or sulphide ores of copper can be melted as efficiently or more efficiently in the electric furnace than in the reverberatory or blast furnaces. 2. The loss of electrodes is small, and the presence of the carbon electrode does not cause enough reduction of iron to be harmful or to increase appreciably the consumption of electrical energy. 3. The losses of copper, gold, and silver by volatilisation would be no greater than they are in reverberatory smelting or ordinary blast-furnace smelting. 4. The cost depends entirely on the nature of the ore to be treated and the relative cost of coal or coke and electrical energy. In general it may be said that from 500 to 700 kilowatt hours per ton of charge would be required for smelting copper ore.

What a Miner can do to Prevent Explosions of Gas and of Coal Dust. By GEORGE S. RICE. Washington: Government Printing Office. 1915.

THE object of this circular issued by the Bureau of Mines is to show the miner how to prevent explosions in coal mines, and what to do to save his own life and the lives of his companions in the event of an explosion occurring. Various recommendations as to the use of pocket flash-lamps, permissible explosives, &c., are made, and the importance of the miner doing all in his power to uphold the authorities and aid them in imposing precautionary measures is emphasised. The circular discusses the precautions necessary to prevent coal-dust explosions, and the various barriers for the purpose in use in France and Germany are shortly described. The notes on self-rescue include some examples from actual disasters which have occurred, and the wide circulation of the pamphlet among miners and mine employees would be advantageous to all concerned.

Metallurgical Smoke. By CHARLES H. FULTON. Washington: Government Printing Office. 1915.

THIS bulletin of the Bureau of Mines is written as far as possible in non-technical language, and the manufacturer or engineer who is interested in the smoke problem at smelting and ore-roasting plants will be able to obtain much useful information from it. Allusion is frequently made to the work which is waiting to be done before the subject is by any means thoroughly elucidated, and the author writes very impartially and fairly. The three main constituents of smoke—gas, flue dust, and fume—are discussed individually and in detail, and methods of recovery, &c., are explained. The author includes descriptions of actual practice as well as of suggested processes, and some account is given of the legal aspects of the smelter-smoke problem.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxi. No. 3, July 19, 1915.

Catalysis of Hydrogen Peroxide in a Homogeneous Medium with Acids and Alkalis.—Georges Lemoine.—The author has already shown that water acts as a catalyst towards hydrogen peroxide, the decomposition being greater the greater the proportion of water present.

By further experiments he has now found that the presence of hydrochloric or sulphuric acid retards the decomposition, while alkalis (potash, soda, lithia) accelerate it. The retarding action of acids is appreciable when some ten-thousandths by weight are present in the total volume of the liquid, and one thousandth part by weight of alkali in the total volume of liquid is sufficient to accelerate the decomposition appreciably.

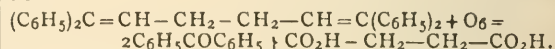
No. 4, July 26, 1915.

This number contains no chemical matter.

Bulletin de la Société Chimique de France.

Vol. xvii.-xviii., No. 8, 1915.

Some Symmetrical Bi-tertiary Glycols.—M. Bouvet.—Tetramethyl-hexane diol, which has been called adipic pinacone, can be prepared by heating together ethereal solutions of methyl magnesium iodide and ethyl adipate. A dichlorhydric ether can be prepared from it by the action of hydrochloric acid gas, and with acetic anhydride and sodium acetate it gives a diacetic ether. Tetramethyl-hexane diene can be obtained by the action of pyridine upon the dichlorhydric ether of tetramethyl-hexane diol. Tetraethyl and tetrapropyl hexane diols may be made by allowing ethyl or propyl magnesium iodide to act on ethyl adipate, and the action of magnesium and bromo-benzene upon ethyl adipate and anhydrous ether to acetic acid gives tetraphenyl-hexane diol, which on dehydration gives tetraphenyl-hexane diene. The oxidation of this hydrocarbon by potassium permanganate yields carbon dioxide, succinic acid, and benzophenone, according to the equation—



MISCELLANEOUS.

Iron and Steel Institute.—The Autumn Meeting of the Institute will be held at the Institution of Civil Engineers, Great George Street, Westminster, on Thursday and Friday, September 23 and 24, 1915, commencing at 10.30 a.m. on Thursday and at 10 a.m. on Friday. The following is the programme of proceedings:—

Thursday, September 23.

10.30 a.m.—General Meeting of Members. Scrutineers will be appointed for the examination of voting papers for election of new members of the Institute. A selection of papers will be read and discussed. The Council will give notice of amendment of by-laws.

1 p.m.—The meeting will be adjourned to 10 a.m. on Friday, September 24.

Friday, September 24.

10 a.m.—General Meeting of Members. A selection of papers will be read and discussed.

The following is the list of papers that are expected to be submitted for reading and discussion:—

Wesley Austin, M.Sc.—“Influence of Oxygen on some Properties of Pure Iron.”

T. H. Byrom — “Note on the Carburisation of Iron at Low Temperatures in Blast Furnace Gases.”

Prof. E. D. Campbell — “Influence of Heat Treatment on the Specific Resistance and Chemical Constitution of Carbon Steels.”

Prof. C. A. Edwards, D.Sc., and H. Kikkawa — “Effect of Chromium and Tungsten upon the Hardening and Tempering of High-speed Tool-steel.”

W. H. Hatfield, D.Met. — “Phosphorus in Iron and Steel.”

Prof. K. Honda and H. Takagi — “The Magnetic Transformation of Cementite.”

R. H. Smith — “Sulphur in Malleable Cast Iron.”

Prof. N. Tschischewski — “Iron and Nitrogen.”

THE CHEMICAL NEWS.

VOL. CXII., No. 2912.

ADDRESS TO THE PHYSIOLOGICAL SECTION OF THE BRITISH ASSOCIATION. MANCHESTER, 1915.

By Prof. W. M. BAYLISS, M.A., D.Sc., F.R.S.,
President of the Section.

The Physiological Importance of Phase Boundaries.

EVEN a hasty consideration of the arrangements present in living cells is sufficient to bring conviction that the physical and chemical systems concerned operate under conditions very different from those of reactions taking place between substances in true solution. We become aware of the fact that there are numerous constituents of the cell which do not mix with one another. In other words, the cell system is one of many "phases," to use the expression introduced by Willard Gibbs.

Further, parts of this system which appear homogeneous under the ordinary microscope are shown by the ultra-microscope to be themselves heterogeneous. These are in what is known as the colloidal state. Some dispute has taken place as to whether this state is properly to be called a heterogeneous one, but it is sufficient for our purpose to note that investigation shows that the interfaces of contact between the components of such systems are the seat of the various forms of energy which we meet with in the case of systems obviously consisting of phases which can be separated mechanically, so that considerations applying to coarsely heterogeneous systems apply also to colloidal systems. Although the phases of a colloidal system cannot be so obviously and easily separated as those of an ordinary heterogeneous one, this can be done almost completely by filtration through membranes, such as the gelatin in Martin's process. To avoid confusion, however, it has been suggested that the colloidal state should be spoken of as "micro-heterogeneous." There are in fact certain phenomena more or less peculiar to the colloidal state and due to the influence of the sharp curvature of the surfaces of the minutely subdivided phase. The effect of this curvature is a considerable pressure in the interior of the phase, owing to the surface tension, and it adds further complexity to the properties manifested by it.

We see, then, that the chemical reactions of chief importance to us as physiologists are those known as "heterogeneous." This class of reactions until comparatively recent times has been somewhat neglected by the pure chemist.

In some of its aspects the problem before us was discussed by one of my predecessors, Prof. Hopkins, as also by Prof. Macallum, but its importance will, I think, warrant my asking your indulgence for a further brief discussion. Permit me first to apologise for what may seem to some of those present to be an unnecessarily elementary treatment of certain points.

It is easy to realise that the molecules which are situated at the interface where two phases are in contact are subject to forces differing from those to which the molecules in the interior of either phase are subject. Consider one phase only, the molecules at its surface are exposed on the one side to the influence of similar molecules; on the other side they are exposed to the influence of molecules of a nature chemically unlike their own or in a different physical state of aggregation. The result of such asymmetric forces is that the phase boundary is the seat of various forms of energy not present in the interior of

the phase. The most obvious of these is the surface energy due to the state of tension existing where a liquid or a gas forms one of the phases. It would lead us too far to discuss the mode of origin of this surface tension, except to call to mind that it is due to the attractive force of the molecules for one another, a force which is left partially unbalanced at the surface, so that the molecules here are pulled inwards. The tension is of course only the intensity factor of the surface energy, the capacity factor being the area of the surface. We see at once that any influence which alters the area of the surface alters also the magnitude of that form of energy of which we are speaking.

This is not the only way in which the properties of substances are changed at phase boundaries. The compressibility of a solvent, such as water, are altered, so that the solubilities of various substances in it are not the same as in the interior of the liquid phase. It is stated by J. J. Thomson that potassium sulphate is 60 per cent more soluble in the surface film. The ways in which the properties of a solvent are changed are sometimes spoken of as "lyotropic," and they play an important part in the behaviour of colloids. We meet also with the presence of electrical charges, of positive or negative sign. These are due as a rule to electrolytic dissociation of the surface of one phase, in which the one ion owing to its insolubility remains fixed at the surface, while the opposite ion, although soluble, cannot wander away further than permitted by electrostatic attraction. Thus we have a Helmholtz double layer produced.

Before we pass on to consider how these phenomena intervene in physiological processes, there is one fact that should be referred to on account of its significance in connection with the contractile force of muscle. Surface tension is found to *decrease* as the temperature rises, or, as it is sometimes put, it has a negative temperature coefficient. This is unusual, but if we remember that the interface between a liquid and its vapour disappears when the temperature rises to the critical point, and with it of course all phenomena at the boundary surface, the fact is not surprising that there is a diminution of these phenomena as the critical temperature is approached.

Perhaps that result of surface energy known as "adsorption" is the one in which the conditions present at phase boundaries make themselves most frequently obvious. Since the name has been used somewhat loosely, it is a matter of some consequence to have clear ideas of what is meant when it is made use of. Unless it is used to describe a definite fact it can only be mischievous to the progress of science.

Permit me, then, first to remind you of that fact of universal experience, known as the "dissipation of energy," which is involved in the second law of energetics. Free energy—that is, energy which can be used for the performance of useful work—is invariably found to diminish, if the conditions are such that this is possible. If we have, therefore, a system in which by any change of distribution of the constituents free energy can be decreased, such a change of distribution will take place. This is one form of the well known "Principle of Carnot and Clausius."

Now, practically any substance dissolved in water lowers the surface tension present at the interface between the liquid and another solid or liquid phase with which it is in contact. Moreover, up to a certain limit the magnitude of this effect is in proportion to the concentration of the solute; therefore, as was first pointed out by Willard Gibbs, concentration of a solute at an interface has the effect of reducing free energy, and will therefore occur. This is adsorption. As an example, we may take the deposition of a dyestuff on the surface of charcoal, from which it can be removed again unaltered by appropriate means, such as extraction with alcohol. Charcoal plus dye may, if any satisfaction is derived from the statement, be called a compound, but since its chemical composition depends on the concentration of the solution in which it

was formed it is much more accurate to qualify the statement by calling it an "adsorption compound." Moreover, the suggestion that the union is a chemical one tends to deprive the conception of chemical combination of its characteristic quality, namely, the change of properties. Dyestuff and charcoal are chemically unchanged by adsorption.

The origin of adsorption from surface tension is easily able to explain why it is less as the temperature rises, as we find experimentally. As we have just seen, surface tension diminishes with increase of temperature.

Let us next consider what will happen if the liquid phase contains in solution a substance which lowers surface tension and is also capable of entering into chemical reaction with the material of which the other (solid) phase consists. For example, a solution of caproic acid in contact with particles of aluminium hydroxide. On the surface of the solid the concentration of the acid will be increased by adsorption, and in consequence the rate of the reaction with it will be raised, according to the law of mass action. Further, suppose that the liquid phase contains two substances which react slowly with each other, but not with the solid phase; they will be brought into intimate contact with each other on the surface of the solid phase, their concentration raised, and the rate of their interaction increased. One of the reagents may clearly be the solvent itself. But in all these cases the rate of the reaction cannot be expressed by a simple application of the law of mass action, since the active masses are not functions of the molecular concentrations but of the surface of the phase boundaries. The application of these considerations to the problem of the action of enzymes and of heterogeneous catalysis in general will be apparent. That the action of enzymes is exerted by their surfaces is shown, apart from the fact that they are in colloidal solution, by the results of experiments made in liquids in which the enzymes themselves are insoluble in the usual sense, so that they can be filtered off by ordinary filter-paper and the filtrate found to be free from enzyme. Notwithstanding this insolubility enzymes are still active in these liquids. The statement has been found up to the present to apply to lipase, emulsin, and urease, probably to trypsin, and the only difficulty in extending it to all enzymes is that of finding a substrate soluble in some liquid in which the enzyme itself is not. That adsorption is a controlling factor in the velocity of enzyme action has been advocated by myself for some years, but it is not to be understood as implying that the whole action of enzymes is an "adsorption phenomenon," whatever may be the meaning of this statement. The rate at which the chemical reaction proceeds is controlled by the mass of the reagents concentrated on the surface of the enzyme phase at any given moment, but the temperature coefficient will of course be that of a chemical reaction.

The thought naturally suggests itself, may not the adsorption of the reacting substances on the surface of the enzyme suffice in itself to bring about the equilibrium at a greater rate, so that the assumption of a secondary chemical combination of a chemical nature between enzyme and substrate may be superfluous? I should hesitate somewhat to propose this hypothesis for serious consideration were it not that it was given by Faraday as the explanation of one of the most familiar cases of heterogeneous catalysis, namely, the union of oxygen and hydrogen gases by means of the surfaces of platinum and other substances. The insight shown by Faraday into the nature of the phenomena with which he was concerned is well known, and has often caused astonishment. Now, this case of oxygen and hydrogen gases is clearly one of those called "catalytic" by Berzelius. The fact that the agent responsible for the effect did not itself suffer change was clear to Faraday. I would also, in parenthesis, call attention to the fact that he correctly recognised the gold solutions which he prepared as suspensions of metallic particles, that is, as what we now call colloidal solutions. Although the systematic investigation of colloids, and the

name itself, were due to Graham, some of the credit of the discovery should be given to the man who first saw what was their nature. Adsorption, again, was accurately described by Faraday, but without giving it a name.

I confess that there are at present difficulties in the way of accepting concentration by adsorption as a complete explanation of the catalytic activities of enzymes. It is not obvious, for example, why the same enzyme should not be able to hydrolyse both maltose and saccharose, as it is usually expressed. Another difficulty is that it is necessary to assume that the relative concentration of the components of the chemical system must be the same on the surface of the enzyme as it is in the body of the solution; in other words, the adsorption of each must be the same function of its concentration. Unless this were so, the equilibrium position on the enzyme surfaces, and therefore in the body of the solution, would be a different one under the action of an enzyme from that arrived at spontaneously or brought about by a homogeneous catalyst such as acid. This consideration was brought to my notice by Prof. Hopkins, and requires experimental investigation. We know, indeed, that in some cases there is such a difference in the position of the equilibrium position, for which various explanations have been suggested, but it would be a matter of some interest to know whether this difference has any relation to different degrees of adsorption of the components of the system.

At the same time adsorption is under the control of so many factors, surface tension, electrical charge, and so on, that the possibilities seem innumerable. There are, moreover, two considerations to which I may be allowed to call your attention. Hardy has pointed out that it is probable that the increased rate of reaction at the interface between phases may be due not merely to increased concentration as such, but that in the act of concentration itself molecular forces may be brought into play which result in a rise in chemical potential of the reacting substances. In the second place, Barger has shown that the adsorption of iodine by certain organic compounds is clearly related to the chemical composition of the surfaces of these substances, but that this relationship does not result in chemical combination nor in abolition of the essential nature of the process as an adsorption. It would appear that those properties of the surface, such as electric charge and so on, which control the degree of adsorption, are dependent on the chemical nature of the surface. This dependence need not cause us any surprise, since the physical properties of a substance, inclusive of surface tension, are so closely related to its chemical composition.

There is one practical conclusion to be derived from the facts already known with regard to enzymes. This is that any simple application of the law of mass action cannot lead to a correct mathematical expression for the rate of reaction, although attempts of this kind have been made, as by Van Slyke. The rate must be proportional to the amount of substrate adsorbed, and this again, is a function both of the concentration of the substrate and of that of the products. It is, then, continuously varying quantity. Expressed mathematically, the differential equation for the velocity must be something of this kind:—

$$\frac{dC}{dt} = KC^n$$

where n itself is an unknown function of C , the concentration of the substrate or products.

The hypothesis of control by adsorption gives a simple explanation of the exponential ratio between the concentration of the enzyme and its activity, which is found to be different numerically according to the stage of the reaction. At the beginning it may be nearly unity, in the middle it is more nearly 0.5, as in the so-called "square root law" of Schütz and Borissov, which is, however, merely an approximation. Simple explanations are also given of the fact that increasing the concentration of

the substrate above a certain value no longer causes an increased rate of reaction. This is clearly because the active surface is saturated. Again, the effect of antiseptics and other substances which by their great surface activity obtain possession of the enzyme surfaces, and thereby exclude to a greater or less degree the adsorption of the substrate, receives a reasonable account. In many cases the depressant or favouring action of electrolytes, including acid and alkali, is probably due to aggregation or dispersion of the colloidal particles of the enzyme, with decrease or increase of their total surface. It is to be noted that such explanations are independent of any possible formation of an intermediate compound between enzyme and substrate, *after* adsorption has taken place.

There is a further way in which adsorption plays a part in the chemical processes of cells, including those under the influence of catalysts. It is a familiar fact that the concentration of water plays a large part in the position of equilibrium attained in reversible reactions of hydrolysis and synthesis. A synthetic process is brought about by diminution of the effective concentration of water. There are doubtless means of doing this in the elaborate mechanisms of cell life, and in all probability it is by adsorption on surfaces which are able to change their "affinity" for water.

I pass on to consider briefly some other cases in which the phenomena at phase boundaries require attention.

Let us turn our gaze from the interior of the cell to the outer surface, at which it is in contact with the surrounding medium. From the nature of adsorption there can be no doubt that if the cell or the surrounding liquid contains substances which decrease surface energy of any form these constituents will be concentrated at the interface. There are many such substances to be found in cells, some of lipid nature, some proteins, and so on. Further, the experiments of Ramsden have shown that a large number of substances are deposited in surface films in a more or less rigid or solidified form. We are thus led to inquire whether these phenomena do not account for the existence of the cell membrane, about which so much discussion has taken place. We find experimentally that there are facts which show that this membrane under ordinary resting conditions is impermeable to most crystalloids, including inorganic salts, acids, and bases. There is no other explanation of the fact that the salts present in cells are not only in different concentration inside from that outside, but that there may be absence of certain salts from one which are present in the other, as, for example, sodium in the plasma of the rabbit not in the corpuscles. Moreover, the experiments of Hoerber have shown that electrolytes are free in the cells, so that they are not prevented from diffusion by being fixed in any way. The mere assumption of a membrane impermeable to colloids only will not account for the facts, since, as I have shown in another place, this would only explain differences of concentration but not of composition. The surface concentration of cell constituents readily accounts for the changes of permeability occurring in functional activity, since it depends on the nature of the cell protoplasm, and chemical changes of many and various kinds occur in this system. If such be the nature of the cell membrane it is evident that we are not justified in expecting to find it composed of lipid or of protein alone. It must have a very complex composition, varying with the physiological state of the cell; indeed, complex artificial membranes have been prepared having properties very similar to that of the cell.

This view, that the membrane is formed by surface concentration of constituents of the cell, readily accounts for the changes of permeability occurring in functional activity, since its composition depends on that of the cell protoplasm, and chemical changes of various kinds take place in this system, as it is scarcely necessary to remind you. In fact the cell membrane is not to be regarded as an independent entity but as a working partner, as it were, in the business of the life of the cell. In the state

of excitation, for example, there is satisfactory evidence that the cell membrane loses its character of semi-permeability to electrolytes, &c. This statement has been shown to apply to muscle, nerve, gland cells, and the excitable tissues of plants, as well as to unicellular organisms. We shall see presently how this fact gives a simple explanation of the electrical changes associated with the state of activity.

If, then, the cell membrane is a part of the cell system as a whole, it is not surprising to find that substances can affect profoundly, although reversibly, the activities of the cell, even when they are unable to pass beyond the outer surface. The state of dynamic equilibrium between the cell membrane and the rest of the cell system is naturally affected by such means, since the changes in the one component involve compensating ones in the other. Interesting examples of such actions are numerous. I may mention the effect of calcium ions on the heart muscle, the effect of sodium hydroxide on oxidation in the eggs of the sea-urchin, and that of acids on the contraction of the jelly-fish. Somewhat puzzling are those cases in which drugs, such as pilocarpine and muscarine, act only during their passage through the membrane and lose their effect when their concentration has become equal inside and outside the cell.

The work of Dale on anaphylaxis leads him to the conclusion that the phenomena shown by sensitised plain muscle can most reasonably be explained by colloidal interaction on the surface of the fibres. The result of this is increased permeability and excitation resulting therefrom.

I referred previously to the electrical change in excitable tissues and its relation to the cell membrane. It was, I believe, first pointed out by Ostwald and confirmed by many subsequent investigators, that in order that a membrane may be impermeable to a salt it is not a necessary condition that it shall be impermeable to both of the ions into which this salt is electrolytically dissociated. If impermeable to one only of these ions, the other, diffusible, ion cannot pass out beyond the point at which the osmotic pressure due to its kinetic energy balances the electrostatic attraction of the oppositely charged ion, which is imprisoned. There is a Helmholtz double layer formed at the membrane, the outside having a charge of the sign of the diffusible ions, the inside that of the other ions. Now, suppose that we lead off from two places on the surface of a cell having a membrane with such properties to some instrument capable of detecting differences of electrical potential. It will be clear that we shall obtain no indication of the presence of the electrical charge, because the two points are equipotential, and we cannot get at the interior of the cell without destroying its structure. But if excitation means increased permeability, the double layer will disappear at an excited spot owing to indiscriminate mixing of both kinds of ions, and we are then practically leading off from the interior of the cell, that is, from the internal component of the double layer, while the unexcited spot is still led off from the outer component. The two contacts are no longer equipotential. Since we find experimentally that a point at rest is electrically positive to an excited one, the outer component must be positive, or the membrane is permeable to certain cations, impermeable to the corresponding anions. Any action on the cell such as would make the membrane permeable, injury, certain chemical agents, and so on, would have the same effect as the state of excitation. If we may assume the possibility of degrees of permeability, the state of inhibition might be produced by decrease of permeability of the membrane of a cell, which was previously in a state of excitation owing to some influence, inherent in the cell itself or coming from the outside. This manner of accounting for the electromotive changes in cells is practically the same as that given by Bernstein.

It will be found of interest to apply to secretory cells the facts to which I have directed your attention. If we

suppose that the setting into play of such cells is associated with the production of some osmotically active substance, together with abolition of the state of semi-permeability of the membrane covering the ends of the cells in relation with the lumen of the alveolus of the gland, it is plain that water would be taken up from the lymph spaces and capillaries and escape to the duct, carrying with it the secretory products of the cells. This process would be continuous as long as osmotically active substances were formed. Such a process has been shown by Lepeshkin to occur in plants and we have also evidence of increased permeability during secretory activity in the gland cells of animals. From what has been said previously, it is evident that electrical differences would show themselves between the permeable and semi-permeable ends of such cells, as has been found to be the case.

As a modifiable structure, we see the importance of such a membrane as that described if it takes part in the formation of the synapse between neurones. The manifold possibilities of allowing passage to states of excitation or inhibition and of being affected by drugs will be obvious without further elaboration on my part.

Enough has already been said, I think, to show the innumerable ways in which phenomena at phase boundaries intervene in physiological events. Indeed, there are very few of these, if any, in which some component or other is not controlled by the action of surfaces of contact. But there is one especially important case to which I may be allowed to devote a few words in conclusion. I refer to the contractile process of muscle. It has become clear, chiefly through the work of Fletcher, Hopkins, and A. V. Hill, that what is usually called muscular contraction consists of two parts. Starting from the resting muscle, we find that it must have a store of potential energy, since we can make it do work when stimulated. After being used in this way, the store must be replenished, since energy cannot be obtained from nothing. This restoration process is effected by an independent oxidation reaction, in which carbohydrate is burnt up with the setting free of energy which is made use of to restore the muscle to its original state. Confining our attention for the moment to the initial, contractile, stage, the essential fact is the production of a certain amount of energy of tension, which can either be used for the performance of external work or be allowed to become degraded to heat in the muscle itself. It was Blix who first propounded the view that the amount of this energy of tension is related to the magnitude of certain surfaces in the muscle fibres. But the fact was demonstrated in a systematic and quantitative manner by A. V. Hill. He showed, in fact, that the amount of energy set free in the contractile process is directly related to the length of muscle fibres, during the development of the state of tension. In other words, the process is a surface phenomenon, not one of volume, and is directly proportional to the area of certain surfaces arranged longitudinally in the muscle. This same relationship has been shown by Patterson and Starling to hold for the ventricular contraction of the mammalian heart and by Kosawa for that of the cold-blooded vertebrate. It appears that all the phenomena connected with the output of blood by the heart can be satisfactorily explained by the hypothesis that the energy of the contraction is regulated by the length of the ventricular fibres during the period of development of the contractile stress. The degree of filling at the moment of contraction is thus the determining factor.

That surface tension itself may be responsible for the energy given off in muscular contraction was first suggested by Fitzgerald in 1878, and it seems, from calculations made, that changes at the contact surface of the fibrillæ with the sarcoplasm may be capable of affording a sufficient amount. The difficulties in deciding the question are great, but, in addition to the facts mentioned, there is other interesting evidence at hand. It has been shown,

by Gad and Heymans, by Bernstein and others, that the contractile stress produced by a stimulus has a negative temperature coefficient. Within the limits of temperature between which the muscle can be regarded as normal, this stress is the greater the lower the temperature. The same statement was shown by Weizsacker (working with A. V. Hill) to hold for the heat developed in the contractile stage. Now, of all the forms of energy possibly concerned, that associated with phase boundaries is the only one with a negative temperature coefficient. Another aspect of this relation to temperature is the well-known increase of the tonus of smooth muscle with fall in temperature.

It is tempting to bring into relation with the change in surface tension the production of lactic acid. In fact, this idea was put into a definite statement by Haber and Klemensievich in 1909 in a frequently quoted paper on the forces present at phase boundaries. The production of acid is stated to alter the electrical forces at this situation. This electrical charge involves a change of surface tension, and it is this change of surface tension which brings about the mechanical deformation of the muscle. Mines also has brought forward good evidence that the production of lactic acid is responsible for the change of tension. As to how the lactic acid is set free, and of what nature the system of high potential present in muscle may be, we require much more information. The absence of evolution of carbon dioxide when oxygen is not present shows that no oxidation takes place in the development of tension. There are other difficulties also in supposing that this system present in resting muscle is of a chemical nature. If the energy afforded by the oxidation of carbohydrate in the recovery stage is utilised for the formation of another chemical system with high energy content, the theory of coupled reactions indicates that there must be some component common to both systems. It is difficult to see what component of the muscle system could satisfy the conditions required. On the whole, some kind of system of a more physical nature seems the most probable. If it be correct that the oxidation of substances other than carbohydrate, fat for example, can afford the chemical energy for muscular contraction, as appears from the results of metabolism experiments, a further difficulty arises in respect to a coupled reaction. But the question still awaits investigation.

On the whole, I think that we may conclude that more study of the phenomena at phase boundaries will throw light on many problems still obscure. It would probably not be going too far to say that the peculiarities of the phenomena called "vital" are due to the fact that they are manifestations of interchange of energy between the phases of heterogeneous systems. It was Clerk Maxwell who compared the transactions of the material universe to mercantile operations in which so much credit is transferred from one place to another, energy being the representative of credit. There are many indications that it is just in this process of change of energy from one form to another that special degrees of activity are to be observed. Such, for example, are the electrical phenomena seen in the oxidation of phosphorus or benzaldehyde, and it appears that, in the photo-chemical system of the green plant, radiant energy is caught on the way, as it were, to its degradation to heat, and utilised for chemical work. In a somewhat similar way, it might be said that money in the process of transfer is more readily diverted, although perhaps not always to such good purpose as in the chloroplast. Again, just as in commerce money that is unemployed is of no value, so it is in physiology. Life is incessant change or transfer of energy, and a system in statical equilibrium is dead.

Potash in the Philippines.—It has been found that the ash of the seaweed collected on the shore of Manila Bay in Tondo yields 15 per cent of potash. An abundant amount of the seaweed, it is asserted, is available.

THE TOUGHENING ACTION OF NITRIC ACID UPON FILTER-PAPERS.

By CLAYTON BEADLE.

WITH the exception of the work done by Francis (*Fourth. Chem. Soc.*, xlvii., 183) nothing of importance appears to have been published on the above subject. Francis states that, to produce the result, either immersion in or moistening with nitric acid at 1.42 sp. gr. and subsequent washing is all that is required, and no precaution is necessary. He also points out that the toughening effect produced by nitric acid differs from that produced with sulphuric acid. He states that filter-paper toughened with nitric acid can be washed and rubbed without damage, like a piece of linen. He gives some results to show the greatly increased strength produced by the treatment. Thus, in a case where the untreated filter-paper broke with a strain of between 100 and 150 grms., after treatment the same paper would stand a strain of 1500 grms. In other words, the toughening by his nitric acid treatment increased the tensile strength more than tenfold. The treated paper, that is paper treated all over in the above mentioned manner, when placed in a funnel, would bear the greatest pressure produced by a common exhausting syringe, whilst a single stroke with the pump broke the untreated paper. In lieu of treating the paper all over, he recommends dipping only the apex of the folded paper into nitric acid. His tests show that the toughened paper contains no nitrogen; it burns like ordinary paper and not like pyroxylin, and instead of increasing in weight it actually decreases. Thus a filter-paper of 11.5 cm. diameter weighed:—

Before treatment	0.6795 grm.
After treatment	0.6749 grm.
= a loss of	0.68 per cent

Wm. R. Rankin in a recent contribution upon the subject appears entirely to disregard the earlier work of Francis. He suggests the following method:—English filter-papers are very quickly dipped in concentrated nitric acid of 1.42 sp. gr., quickly drained, placed in running water, and afterwards in ammonia water of 0.5 per cent, where it is allowed to remain some little time to neutralise the acid completely, after which the paper is washed, drained, pressed between blotting-paper, and finally dried at 100° C. Rankin's suggested method is unnecessarily complex and seems to leave entirely out of account what is already common knowledge. Moreover, Rankin states that some nitration takes place.

To Francis is due the credit of first having suggested dipping only the apex in the acid, also of demonstrating the general advantages of treating filter-paper with nitric acid.

We believe that Mr. E. J. Bevan was the first to use a more simple process than that devised by Francis. He made use of the following procedure:—After the filter-paper had been folded and inserted in a dry funnel in the usual manner, a few drops of nitric acid of 1.42 sp. gr. were allowed to fall on the apex of the paper without touching the sides. The funnel was then canted and quickly rotated so as to saturate a sufficient area, and then immediately held under a tap of running water, then filled and emptied a few times by filling up from the tap and pouring the water out of the top of the funnel, when it is ready for use. If necessary a little distilled water was then passed through to remove any tap-water.

The writer, to whom Mr. Bevan demonstrated this method about thirty years ago, has since used it repeatedly for determinations where a filter-pump has to be used.

It results in toughening of the apex of the paper only; that is, it toughens only the centre portion. This is quite sufficient for most purposes; in other words, it is sufficient to toughen only that portion which does not come in close contact with the glass of the funnel; i.e., the unsupported portion of the paper. The body of the filter-paper

which is in close contact with the glass does not require toughening even when a filter-pump is used.

Fuming nitric acid of 1.52 sp. gr. may be used when the centre only is toughened *in situ*, but cannot be employed when the whole filter-paper is nitrated, nor does it appear to be applicable when the apex is dipped in the acid. There does not, however, appear to be any advantage in the use of fuming nitric when apex is toughened *in situ*.

The dipping of the apex of the paper into the acid, as employed by Francis, before inserting the paper in the funnel does not appear to give any different result from that employed by us, viz., pouring a little acid into the paper *in situ*. The latter method has the advantage of being more simple and expeditious.

Francis in his paper says practically nothing about the question of filtration, but he leaves the impression that the rate of filtration is not materially influenced by this toughening all over process with nitric acid. For the purpose of determining the effect of toughening by nitric acid upon the rate of filtration we employed a Swedish make Muncktel's No. 1 F, filter-papers of 11 cm. Untreated paper (a) was used for the purpose of comparison. Another paper (b) was toughened all over with nitric acid by placing the paper in a dry shallow dish and quickly pouring over it sufficient nitric acid of 1.42 sp. gr. to cover it, and after a few seconds rapidly filling the dish with water, and, after washing with more water for a few times, leaving to soak in fresh water. After washing, the excess of water was removed by placing between blotting-paper and gently pressing. The paper was then folded and inserted in a funnel in the usual manner. The rate of filtration of this paper (b), prepared as above, was measured against the blank (a). Comparative tests were made, first of all, with water at ordinary room temperature (15° to 20° C.) when it was found that the rate of filtration of (a) was just five times that of (b). In other words, the toughening process had resulted in the reduction of the rate of filtration to one-fifth that of normal untoughened paper. Thus, when 100 cc. had passed through untoughened paper (a) only 20 cc. had passed through toughened paper (b). The relative figures were almost the same for boiling water used immediately afterwards (100:25).

By taking the same make of filter-paper and toughening the apex only in the manner employed by us, by placing the paper in the funnel before applying the acid paper (c), we were surprised to find that not only was there no retardation as the result of toughening the apex, but the rate of filtration was very much accelerated. When, however, boiling water was subsequently used upon the same paper (c) the rate of filtration was almost the same as that of the blank paper (a). Subsequent to this, paper (c) was used for a third time but with cold water, when it was found that relative rates of filtration between (a) and (c) were practically the same. In the accompanying table the rates of filtration are expressed in comparison with cold water; i.e., where hot they are corrected to cold. They merely show the relative rates between the blank (a) and the toughened samples.

Paper.	Treatment.	Water used.	Relative rate of filtration, blank with cold water = 100.
			Cc.
(a)	Untoughened	Cold ..	100
(b)	Toughened all over ..	Cold ..	20
(b)	Toughened all over ..	Hot ..	25
(c)	Toughened on apex <i>in situ</i>	Cold ..	200
(c)	Toughened on apex <i>in situ</i>	Hot ..	95
(c)	Toughened on apex <i>in situ</i>	Cold ..	100

Similar experiments were tried with an English-made filter-paper (J. Green, No. 604, Cm. 11), and the results were, relatively speaking, of a similar order to those obtained with the Swedish filter-papers.

It is evident from the above results that to toughen the paper all over not only entails extra manipulation and a larger quantity of acid but also enormously decreases the

rate of filtration, whereas the toughening of the apex only *in situ*, when freshly done and immediately applied when using cold water in the manner above described, increases the rate of filtration, but that the rate of filtration is brought to its normal figure when hot is used.

THE ANALYSIS OF PLATINUM.*

By F. MYLIUS and A. MAZZUCHELLI.

(Continued from p. 135).

CASE A.—PROXIMATE ANALYSIS OF COMMERCIAL PLATINUM.

(a) *Collective Separation of the Constituents.*—1. *Solution.*—10 grms. of the broken-up metal are warmed with 10 grms. of concentrated nitric acid and 100 grms. of hydrochloric acid (about 28 per cent, sp. gr. = 1.14) in a long-necked quartz glass flask to about 40°. Solution is thus quickly effected. After the violent evolution of gas has subsided the temperature is increased to 100°, 20 grms. of nitric acid being gradually added.

The solution is evaporated in a porcelain dish on the water-bath with 6 grms. of pure sodium chloride. After the repeated addition of some water to the dry residue the evaporation is repeated till the acid is driven off; the impure sodium platinum chloride is then heated to 120° for an hour.

2. *Residue.*—The anhydrous brownish hydrochloric acid residue is dissolved in about 100 cc. of cold water. The undissolved residues which are only small are filtered off and washed on the filter with water. They may contain gold, silicates, iron salts, silver chloride, and other substances, and are subjected to a special separation by themselves, by which the preparation of the metallic constituents is effected; they are converted into chlorides, and as far as they are soluble they are added to the filtered original solution. This often leads only to the detection of a trace of gold or silver, which is easily done. In this way gold can be almost completely separated if only about 10 per cent of it is present in the platinum.

3. *Hypobromite Precipitation.*—The filtered original solution is diluted to 500 cc. with water and placed in a platinum dish.

(NOTE.—If no pretensions to great accuracy are made a porcelain dish is allowable and also a flask of good glass instead of a quartz flask for the solution of the metal).

Then 0.8 grm. of pure sodium bicarbonate is added, the solution is warmed to boiling, and then allowed to cool. When litmus-paper is dipped into the liquid it must show a faintly alkaline reaction. Any precipitate which results is ignored and an oxidising agent is added, viz., a solution of 0.8 grm. of sodium bicarbonate in 20 cc. of saturated bromine water; the mixture at once turns blackish.

The dish is now warmed on a water-bath until (on gently stirring) the originally colloidal precipitate thickens to form a black flocculent precipitate, which rapidly settles in the solution, which has now become yellowish red. At the most the separation takes only a few minutes. Here also the reaction of the solution must be feebly alkaline; the nearer it is to neutrality the more complete is the separation of foreign oxides. A strongly alkaline reaction is, however, to be avoided, because under its influence an undesired decomposition of the platinum chloride may take place gradually, with formation of sodium chloride and separation of yellow sodium platinum oxide; the liquid then darkens and the reaction changes from alkaline to faintly acid. In the conditions stated this hydrolytic reaction is limited to a small amount, which keeps the percentage of platinum in the precipitate to a small effective amount.

(If warming the liquid does not lead to the separation of the black precipitate, which remains colloiddally suspended, within half an hour, a little sodium hypobromite is added to the still faintly alkaline solution after cooling, and then after about ten minutes some cubic centimetres of alcohol are added, and the liquid is warmed till it boils gently; coagulation then always takes place).

After it has been proved (before the addition of alcohol) that the addition of more oxidising agent causes no further darkening of the yellow solution, the black precipitate is filtered off and washed with water till the filtrate is quite colourless (if the washing is continued unnecessarily the precipitate may dissolve again colloiddally, giving a blue coloration).

The filtrate is then (as before) boiled with alcohol in order to complete the separation of foreign substances by reduction; the precipitate, which readily settles, is collected on a special filter and added to the principal precipitate.

The filtrate is now evaporated to dryness after the addition of some hydrochloric acid (in order to destroy the bromate).

The residue from a little adulteration of sodium platinum chloride containing sodium chloride can then be used for the purification of this compound (as in case B) and for the isolation of any small impurities still present (see *prox.*), if it is not regarded as preferable to neglect them altogether; in proximate analysis this is allowable because the error (supposing the "clearing" to be good) does not amount to much more than 0.1 per cent of the platinum.

(b) *Analytical Investigation of the other Constituents.*—The other constituents which have been separated together in the form of oxides always contain some platinum as well as small quantities of combined soda.

Their quantitative analysis may conveniently be performed according to the following scheme, which shows some deviations from the process of qualitative analysis (see *ante*).

4. *Ammonium Chloride Precipitation.*—The blue-black oxide precipitate (*cf.* above) is washed with water from the filter into a porcelain dish, and repeatedly evaporated with concentrated hydrochloric acid, finally with addition of nitric acid till the solution has lost its blue colour and become yellowish brown.

(NOTE.—The filter, which still retains its blue colour, can easily be extracted with dilute hydrochloric acid containing a little hydrazine; the hydrazine is again destroyed by evaporation with nitric acid).

The slightly acidified residue from evaporation (which at the most contains less than 0.4 grm. of metal) is dissolved in 6 to 8 cc. of water and thoroughly stirred with 1 grm. of ammonium chloride. The greater part of the iridium, platinum, and palladium is thus precipitated as ammonium double chloride, filtered off, and washed with a very little semi-saturated ammonium chloride solution. To extract the metals still present in the solution the filtrate is evaporated to dryness with 1 cc. of dilute nitric acid. If the salt residue is now extracted with the quantity of dilute nitric acid which is just necessary for solution the further precipitate of the double salts of these metals remains behind and can be collected on a special very small filter. Any ammonium rhodium chloride still clinging to these salts can be washed, with the still more easily soluble double chlorides of copper and iron, by means of a semi-saturated solution of ammonium chloride in dilute nitric acid until the solution runs through colourless.

The contents of the two filters may contain a little rhodium, gold, iron, &c., besides the ammonium double chlorides of iridium, platinum, and palladium; it is, therefore, best to recrystallise (by dissolving in hot water and evaporating the solution with the addition of ammonium chloride and nitric acid) before treating it according to section 10.

* *Zeitschrift für Analytische Chemie*, lxxxix., 1.

CHLORIDE SOLUTION OF THE OXIDES.

Precipitation with ammonium chloride.

Filtrate evaporated with HNO_3 .		Precipitate I.: Ir, Pt, Pd, (Ru).		Ignited and extracted with dilute aqua regia.	
Filtrate: H_2S in the cold.		Precipitate II.: Ir.		Residue: Iridium (Ru).	Filtrate evaporated + NH_4Cl .
Precipitate III. ignited in air, extracted with formic acid.		Filtrate with H_2S and warmed.		Precipitate: Platinum.	Filtrate + $\text{Hg}(\text{CN})_2$: Palladium.
Blue filtrate: Copper.	Residue as chloride soluble in ether: Gold.	Precipitate ignited: Rhodium.	Filtrate oxidised and precipitated with ammonia.		
Precipitate ignited: Iron.			Filtrate acidified + potassium ferrocyanide. Precipitate: Zinc, Cobalt, Nickel.		

5. *Sulphide Precipitation.* (a) *Copper, Gold.*—The filtrate containing ammonium chloride is evaporated to dryness with hydrochloric acid and thus freed from nitric acid. The residue is dissolved in about 30 cc. of water, two or three drops of hydrochloric acid are added, and for a few seconds sulphuretted hydrogen is led in till the cold liquid smells strongly of it. The copper sulphide thus precipitated is at once filtered after coagulation and washed with water.

The precipitate is ignited in the air, the oxide obtained as the product of ignition is weighed and dissolved in dilute nitric acid.

(NOTE.—If the presence of other heavy metals like lead, bismuth, &c., besides copper, is suspected, the precipitated sulphide is dissolved in nitric acid and treated according to the usual analytical process).

The small insoluble portions in it consist of noble metals, and especially of rhodium or a trace of gold, and by subtracting them the amount of copper oxide is obtained. (If the amount of copper is very small it is advisable to determine it colorimetrically in ammoniacal solution). The metallic residue is treated with dilute aqua regia, which dissolves gold and leaves the rhodium behind.

6. *Sulphide Precipitation.* (b) *Rhodium.*—If rhodium is present it is revealed by the red coloration of the filtrate when freed from copper, &c. After the sulphuretted hydrogen has been driven off its amount may be roughly estimated by colorimetric comparison with hydrochloric acid rhodium solutions of known composition. If larger quantities are present it is best to isolate them by the crystallisation of the red ammonium rhodium chloride, which dissolves in water easily but in saturated ammonium chloride solution with difficulty (after the iridium and platinum ammonium chloride have been thoroughly separated). By the ignition of the double salt in hydrogen the metal is thus obtained in a state of sufficient purity. With small quantities of rhodium this is not necessary. In this case by warming the solution with sulphuretted hydrogen for hours the metal must be separated as sulphide, together with any traces of iridium, &c., still present. The metal obtained from the isolated sulphide by ignition is to be regarded as "raw rhodium," for on heating with fused potassium bisulphate it is only partly dissolved. But by evaporation with dilute aqua regia the sulphide precipitate is readily converted into chloride solution (containing sulphate) which is suitable for purification in the wet way. It must be emphasised that all known methods of separating rhodium from iridium, &c., are incomplete, inasmuch as they do not allow of the precipitation of all the rhodium in a purified state.

If no unknown metals precipitated as sulphide are present the degree of purity of the rhodium isolated is greater the more carefully the platinum and iridium have originally been removed as ammonium chloride compounds. To

establish rules for the determination of traces of rhodium in technical platinum would require very detailed experiments.

7. *Ammonia Precipitation. Iron.*—The filtered solution after treatment with sulphuretted hydrogen still contains the metals of the iron group. After the solution has been warmed, oxidised, and strongly diluted the iron is precipitated as usual with ammonia. The ignited and weighed iron oxide is said to be pure, but as a matter of fact it usually contains traces of iridium, &c., which had escaped the earlier precipitations. In the extract made with 28 per cent hydrochloric acid the iron can be determined colorimetrically, while the residue can be looked upon as iridium if there are no other indications. In more accurate determinations it is advisable to dissolve the ammonia precipitate in dilute hydrochloric acid, and to shake up the iron chloride repeatedly with ether; the aqueous layer which contains the impurity is then treated according to 8.

8. *Ferrocyanide Precipitation. Zinc, Nickel, Cobalt.*—If a specimen of the ammoniacal filtrate is acidified with hydrochloric acid and potassium ferrocyanide is added, the appearance of a turbidity shows the presence of nickel, cobalt, or zinc. (Cobalt is sometimes present in the solution as red purpureo-cobalt chloride and must not be confused with rhodium). Generally, nickel (cobalt) is present in traces. The much concentrated filtrate of iron is made faintly ammoniacal and saturated with sulphuretted hydrogen in the warmth, and then made feebly acid with hydrochloric acid. Nickel (cobalt) sulphide is then precipitated. After being filtered and washed it is ignited in air and then in hydrogen. On solution in aqua regia any trace of iridium precipitated with it would be left behind.

9. *Ignition Test.* If the test with potassium ferrocyanide has given a negative result the ammoniacal filtrate should quite volatilise on evaporation and further ignition, giving only a small quantity of sodium chloride (sulphate). If the small residue left behind is not quite soluble in water earthy substances are present, which arise chiefly from the vessels. Here also a trace of iridium can be recognised.

10. *Palladium.*—Finally, the ammonium chloride precipitate containing iridium, palladium, and platinum is to be investigated (prepared according to No. 5). The small residues obtained as "iridium" in other operations are added to the principal precipitate.

The filters are ignited, and the ammonium chloride compounds are decomposed by cautious heating; the residue is finally heated for a few minutes in hydrogen to a white heat.

The metal is extracted in a covered porcelain dish with a mixture of one part of aqua regia and three parts of water at the temperature of the water-bath, the yellow solution being poured off from time to time. When the

sintered metal has formed a powder and fresh dilute aqua regia is hardly coloured appreciably (iridium), the extraction is stopped and the iridium filtered off. In the filtrate only a little iridium is present besides palladium and platinum.

After evaporation a concentrated chloride solution free from nitric acid is prepared, from which the platinum containing iridium is precipitated by saturation with ammonium chloride. From its colour an estimate can be made whether it is worth while to isolate the iridium contained in it; the way to do it is to ignite again and extract with much diluted aqua regia (1:5), this time at 50° at the highest.

By evaporation of the filtrate containing ammonium chloride, precipitation with sulphuretted hydrogen in the cold, and ignition of the sulphide in hydrogen, palladium is obtained. After weighing it can be dissolved in nitric acid and if necessary purified by precipitation with mercury cyanide.

11. *Iridium*.—All the iridium is strongly ignited in hydrogen and weighed. In consequence of the increased density it is now insoluble even in concentrated aqua regia.

The metal may contain a little ruthenium. In order to test for it, it is heated to a faint red heat in a gold crucible with potassium nitrate and potash. On treatment of the melt with water a dark liquid is obtained, from which blue iridium dioxide slowly separates in a test-tube. If the cleared supernatant liquid is blue (owing to iridium) no appreciable amount of ruthenium is present (Rose-Finkener, II., p. 254); in its presence the solution would be greenish, as pure ruthenium colours potash melts decidedly yellow. For the quantitative determination of ruthenium it would be necessary to treat the solution and precipitate separately with sodium hypochlorite, and to distil off the per-ruthenic acid in a current of chlorine (Deville).

(NOTE.—The determination of ruthenium can conveniently be performed with a special specimen of platinum metal).

The iridium dioxide produced in the fusion process may be dissolved by concentrated hydrochloric acid (aqua regia). Any residue obtained may contain earthy admixtures.

(To be continued).

THE VAPOUR PRESSURE OF CONCENTRATED SUGAR SOLUTIONS.*

By D. ORSON WOOD, B.Sc., A.R.C.Sc.

(Concluded from p. 137).

The Osmotic Pressure.—It is not to be expected that accurate values of the osmotic pressure can be deduced from vapour pressure observations, since the calculation requires in effect an accurate knowledge of the depression $\pi_0 - \pi_\pi$, and therefore any error in π_π has a considerable influence on the final result. Nevertheless, since no experimental values have been obtained with solutions approaching the concentrations used here or at the temperatures of these experiments it is of some interest to attempt the calculation.

Porter (*Proc. Roy. Soc.*, 1907, lxxix., A) has developed the exact relation which connects the osmotic pressure and the vapour pressures of the solution and solvent. He gives it in the form—

$$\int_{\pi_\pi}^{\bar{p}} s d\bar{p} = \int_{\pi_\pi}^{\pi_0} v d\bar{p} + \int_{\pi_0}^{\bar{p}-P} u d\bar{p};$$

where, in addition to the symbols already used,—

s = "shrinkage" in the volume of the solution when 1 gm. of solvent is removed from an infinite volume.

u = specific volume of the liquid solvent.

v = specific volume of the solvent vapour.

$\bar{p}$ = hydrostatic pressure on the solution.

P = osmotic pressure of solution when it is under the pressure $\bar{p} = \bar{p} - \pi_0$ when the solvent is under its own vapour pressure.

To integrate this we will assume that the liquids are incompressible—that is, s and u independent. To integrate this we will use Callendar's gas equation—

$$v = \frac{RT}{\bar{p}} - c + b,$$

which has been shown to represent the behaviour of water vapour with considerable accuracy. In this equation b is a constant volume of the order u , while c depends on the temperature, being equal to $c_0 \left(\frac{T_0}{T}\right)^{3.33}$, and for the temperatures dealt with here is of the order of 30 cc. To allow for the compressibility of the liquid we write—

$$s = s_0(1 - a\bar{p}),$$

and in the small correcting term so introduced put a equal to the compressibility of water.

Integrating and rearranging, we have at once—

$$P \bar{p} s \left(1 - \frac{aP\bar{p}}{2}\right) = RT \log_e \frac{\pi_0}{\pi_\pi} - c(\pi_0 - \pi_\pi) + (b - s)(\pi_0 - \pi_\pi),$$

the term involving u vanishing when the limits are inserted. The suffix in the term $P\bar{p}$ will be dropped, it being noted that the osmotic pressure dealt with is that at T° C. when the solvent is under its own vapour pressure. In applying the equation, even to the present case, the first term on the right alone is important, and it is certainly permissible to drop $(b - s)(\pi_0 - \pi_\pi)$, since both b and s are nearly equal to 1.

The shrinkage s is by definition equal to $\left(\frac{\partial V}{\partial M}\right)_m$;

where V is the total volume of a solution made up of M gm. of solvent and m of solute. It can be calculated from this expression, but a form given by Callendar (*loc. cit.*) is more convenient. It is—

$$s = v - c \frac{dv}{dc},$$

where v is the specific volume of the solution and c , the concentration, is equal to m/M . This requires a knowledge of the density of the solution for different concentrations at each temperature for which P is to be calculated. Landolt and Börnstein give results obtained by Plato (*Abhdl. Norm. Eich.-Komm.*, 1900, ii., 140) up to 60° C., so that as far as this temperature the data for s are known. Above this its value must be found by extrapolation. It was observed that, for a given value of c , dv/dc showed no certain change with temperature from 20° to 60° C., so that s within this range was less than v by a certain constant volume. It was assumed that this constant difference was maintained up to 90° C.

As a sample calculation we have for solution I at 60° C.—

$$\begin{aligned} P \left(1 - \frac{0.000041P}{2}\right) &= \\ &= \frac{8.315 \times 10^7 \times 333 \times 2.303 \times 0.0212}{18 \times 1.013 \times 76 \times 981 \times 13.59} - \frac{38.68 \times 0.71}{1.013 \times 76} \\ &= 73.16 - 0.36 \\ &= 72.8, \end{aligned}$$

or—

$$P = 72.8 + 0.0000205 \times 72.8^2 = 72.8 + 0.1 = 72.9 \text{ atmos.}$$

The values of P given in Table VIII. were calculated in this way. Those in square brackets are deduced from values of $\log \pi_0/\pi_\pi$ taken from a straight line drawn through the points obtained by plotting the ratio against T . The others are calculated from the vapour pressures read off from the curves.

* A Paper read before the Faraday Society, May 11, 1915.

TABLE VIII.

Temperature, °C.	S.	$\frac{RT}{S} \log_e \frac{\pi_o}{\pi_\pi}$	$-\frac{C}{S} (\pi_o - \pi_\pi)$	$\frac{dP^2}{2}$	P.
Solution I.					
60	1.013	73.16	-0.36	+0.11	72.9
70	1.019	78.83 [80.25]	-0.52	+0.13 [+0.13]	78.4 [79.8]
80	1.026	82.73 [86.35]	-0.78	+0.11 [+0.15]	82.1 [85.7]
90	1.032	93.01	-1.05	+0.18	92.2
Solution II.					
60	1.006	186.4 [183.2]	-0.9	+0.7 +0.7	186.2 [183.0]
70	1.013	175.9 [182.9]	-1.2	+0.6 [+0.7]	175.3 [182.4]
80	1.020	180.3	-1.6	+0.6	179.3
90	1.025	178.5	-1.9	+0.6	177.2
Solution III.					
60	1.001	316.8	-1.5	+2.4	347.7
70	1.008	337.4	-2.1	+2.3	337.6
80	1.015	312.6 [326.1]	-2.6	+2.0 [+2.2]	312.0 [325.7]
90	1.020	315.0	-3.5	+2.0	313.5

It will be seen that for II. and III. the calculated value of the osmotic pressure has a distinct tendency to diminish with rise of temperature and not to increase, a result sufficiently unexpected to merit a little theoretical consideration apart from the question of the accuracy of the observations on which the calculations are based. It has been firmly established that these sugar solutions warm when they are diluted adiabatically, so that according to Kirchhoff's equation, and quite independently of the results recorded in this paper, $\log_e \pi_o/\pi_\pi$ would decrease as the temperature rises, while at the same time the c term becomes increasingly negative. If therefore the logarithm decreases faster than the temperature increases the osmotic pressure must decrease.

If we were to accept the suggestion that negative heats of dilution imply an association of solute molecules, the amount of which becomes greater at the higher temperatures, then the dynamical explanation would be that the increased association more than balanced the increase of kinetic pressure due to the rise of temperature. On the other hand, if Callendar's hydration factor a changes owing to the formation of simpler hydrates at the higher temperatures, then one might consider the increase in the effective dilution due to the liberation of the water previously attached to the sugar molecules to be responsible for the decrease in the osmotic pressure.

Some years ago, when Berkeley and Hartley first published their measurements of the osmotic pressure of strong sugar solutions, Prof. Porter found that their results could be represented fairly well by the equation—

$$P = \frac{nR_oT}{V - nb},$$

where n is the number of sugar molecules in V cc. of solution and R_o is the universal gas constant. In this expression b will be of the order of the volume of 1 gram molecule of sugar together with its attached water molecules. Substituting Berkeley and Hartley's values of P , we find b to come out approximately equal to 280 cc.; the values of P , shown in Table VIII., calculated for solutions of much greater concentration and at considerably higher temperatures (90° instead of 20°) give the same result. This supports the belief that the mean values of the osmotic pressures given in this paper for each solution are reasonably correct even if the variation with tempera-

ture is not. It leads also to an interesting check on the calculations; for example, for solution II. at 60° C., $a=4.51$ and b works out to be 283 cc.; at 90° C., $a=3.60$ and $b=265$ cc.; thus the volume of the sugar molecule has apparently decreased by 18 cc. while a has diminished by 0.91 molecule, or 16.5 cc.

(NOTE.—If b be assumed to be equal to the volume of the hydrated molecule in the solution, then for solution II. at 60° C. this volume (283 cc.) is 68 cc. greater than that of the sugar molecule alone (215 cc.). This difference is equal to the volume of 3.8 water molecules instead of 4.5, a good agreement in view of the fact that some shrinkage would be expected to take place).

Differentiating the equation for P with respect to T , we obtain—

$$\frac{dP}{dT} = \frac{P}{T} \left(1 + \frac{P}{R_o} \frac{db}{dT} \right)$$

which makes P independent of the temperature when $\frac{db}{dT} = -\frac{R_o}{P}$. This means that when $P=180$ atmospheres, as it does for solution II., a loss of 1 molecule of water for each 40° C. rise of temperature would suffice. A greater rate of dehydration than this would involve a decrease of the osmotic pressure with rise of temperature.

It is probable, however, that this stage is not reached in the present case, and that the real osmotic pressure does not diminish in the manner shown in Table VIII., for it will now be shown that the manner in which the calculated values change is due to the too rapid variation in the experimental values of $\log \pi_o/\pi_\pi$ with temperature.

Writing—

$$P_s = RT \log_e \frac{\pi_o}{\pi_\pi}$$

and assuming R to be independent of temperature, we have—

$$\frac{\partial}{\partial T} (P_s) = RT \frac{\partial}{\partial T} \left(\log_e \frac{\pi_o}{\pi_\pi} \right) + R \log_e \frac{\pi_o}{\pi_\pi}.$$

For P_s to be independent of T , $\frac{\partial (P_s)}{\partial T} = 0$. Substituting

for $\frac{\partial}{\partial T} \left(\log_e \frac{\pi_o}{\pi_\pi} \right)$ from Kirchhoff's equation, we then obtain—

$$\frac{H}{T} = -R \log_e \frac{\pi_0}{\pi_\pi}, ^\circ$$

a special equation for the latent heat of dilution which holds approximately only when the osmotic pressure is independent of temperature, the change in s being quite small (2 per cent in 30° C.). For solution II. at 60° C. the value of $-RT \log_e \pi_0/\pi_\pi$ is -4.44 , whereas Kirchhoff's equation applied to the same data gives $H = -5.16$, a value which corresponds to a slow diminution of P with rise of temperature. Reasons have been given in the section on latent heat of dilution for supposing that the true value of the latent heat is smaller than this, so that the correct conclusion to be drawn from the calculations is that at higher temperatures with these strong solutions P alters very slowly with temperature.

The latent heat of dilution can be calculated from the osmotic pressure from the following equation due to Porter (*Trans. Faraday Soc.*)—

$$\frac{H}{T} = (s-u) \frac{\partial}{\partial T} \left(\frac{\pi}{T} \right) + u \frac{\partial}{\partial T} \left(\frac{P}{T} \right),$$

where all the symbols have their previous meaning. This formula was applied to calculate H from the results of Morse and his assistants, already mentioned, the $(s-u)$ term being neglected. Applied to the present case it gives H at 60° C.—

For solution II. = -5.62 cal./grms.

For solution III. = -15.9 cal./grms.

—values which agree well with those calculated directly from Porter's modification of Kirchhoff's equation.

Summary and Conclusion.

1. A static method suitable for the determination of the vapour pressure of highly concentrated solutions is described.
2. Measurements of the vapour pressures of three sugar solutions, of strength varying from 48 to 69 per cent, are given.
3. These results are shown to lead to values of the latent heat of dilution of the right sign and order.
4. Their bearing on the hydration theory is discussed, and Callendar's hydration factor a is shown to vary regularly through the value 4.
5. The vapour pressures are used to calculate the osmotic pressure, which, while of the right order, is found to have a tendency to diminish with rise of temperature. This result is considered theoretically, and it is concluded that, while it is probable that the real osmotic pressure does not diminish, yet it certainly changes very slowly with temperature in the case of these strong solutions.

In conclusion, I must express my very great gratitude to Prof. Porter for his unwearied kindness and attention throughout the whole course of this work.

Use of Aluminium as Anti-tartar in Steam Boilers.

—I. Pouget.—It is well known that laboratory water-baths which are furnished with constant level arrangements become covered with a layer of tartar, which finally completely obstructs the feed tube. The author has found that apparatus which is painted on the inside with aluminium paint can be used almost continuously for three years without being cleaned. The presence of aluminium metal prevents the formation of a deposit of tartar, and it is best employed in the form of paint made by mixing aluminium powder with oil of turpentine containing resin.—*Comptes Rendus*, clxi., No. 6.

* On looking through Callendar's paper after this expression had been obtained, it was found that, giving an equation similar to this, he contemplates a possibility of P being independent of but not diminishing with T .

NOTICES OF BOOKS.

Recapture and Expansion of British Trade. Chemical and Allied Trades. London: International Correspondence Schools, Ltd.

This pamphlet is intended for the use of men engaged in chemical and allied trades, who are students of the International Correspondence Schools, Ltd., as a supplement to the regular instruction papers. In case any readers of the *CHEMICAL NEWS* are not acquainted with the excellent work of the Correspondence Schools it may be well to explain that the object of the organisation is the instruction of men who are anxious to study in their spare time in order to make themselves more efficient and useful to their employers. The average age of the students is twenty-seven, and practically all of them are wage earners. During the past six years more than 150,000 men employed in the great industries have been enrolled as students, and the work which is being done by the Schools is of very great value and importance to the nation. This special paper aims at educating and informing the students on some of the vital factors underlying the maintenance of British trade supremacy. Certain facts and statistics have been collected, and the inferences to be drawn from them are clearly shown, what may be described as the text being Mr. Lloyd George's statement: "We have been employing too much of the haphazard, leisurely, go-as-you-please methods which, believe me, would not have enabled us to maintain our place as a nation, even in peace, much longer." The spirit in which the pamphlet is written appears to us to be excellent, as the following quotations and extracts from it will show. In the introduction is to be found a frank recognition of our negligence in the past, and of the fact that Germany's success in trade is to be ascribed to her strenuousness and great enterprise. Various trades are discussed in some detail, beginning with the beet-sugar industry, which is considered first because of the great opening for it in Great Britain and also because it would establish in England a huge agricultural industry, providing profitable employment for a very large number of workers of all classes. It is pointed out that 75 per cent of our total sugar imports consists of continental beet-sugar, and of this 80 per cent (or three-fifths of our total consumption) came from Germany and Austria alone. It has been proved by experiments made on a working scale that sugar-beet can be grown in this country containing the same percentage of sugar as the continental beet, and the yield per acre is as great as, or greater than, at continental centres, and if sugar factories could be established in country districts close to the source of the beet supply, and Government assistance could be obtained for them at any rate for a time, a great industry could undoubtedly be established. It is idle to deny that there are certain difficulties to be overcome, but they are by no means insurmountable and are quite out of proportion to the national benefit which would accrue. It has, moreover, been shown that, if properly carried out, beet growing in rotation enriches the soil and the waste products have considerable value as a cattle food. In passing it may be mentioned that it is perhaps rather misleading to speak of the dried pulp as a "source" of potash.

The next industry discussed is that of the coal-tar dyes, and the familiar story of Britain's slackness and failure to grasp opportunities is well told. Allusion is made to the great need for novelties evolved by the trained chemist of artistic and original ideas; practically any price can be obtained for a new shade or tint, and especially in the dyeing industry novelties pay best. The oil-cake industry is another example of the lack of enterprise of Great Britain and her failure to utilise the services and knowledge of technically trained men. In 1913 we exported £1,250,000 of bran and other grain refuse, of which £521,000 went to Germany, while we imported from Germany over £400,000 worth of oil-cake. Thus, while our exports of feeding stuffs are chiefly refuse

Germany's principal export is the manufactured article—oil-cake. The British manufacturer has now an unrivalled chance not only of producing oil-cake and feeding-stuffs for home use, but also of capturing the foreign markets for these substances, which have hitherto been supplied by Germany. In the section on the pottery trade it is shown that British firms are to be severely blamed for their carelessness in packing and their inattention to details in connection with the despatch of goods. In the glass industry also there is a great opportunity of expanding our trade, and it has not been allowed to slip, for there are now being placed on the market British-made flasks, beakers, &c., which have been thoroughly tested and found to be as good as the best German makes, while the price is not unduly high and should soon be able to be reduced. The outlook in the paper trade also is most encouraging, and some of the leading firms have shown themselves to be fully alive to their opportunities and have been most enterprising, as, for example, in taking up the manufacture of filter-paper, which has previously been made chiefly in Germany. Other industries discussed are the manufacture of painters' colours and materials, chemicals, photographic materials, and leather substitutes. Metallurgy is treated in outline only, being the subject of another pamphlet. The statement of the Australian Attorney-General is quoted, viz., that German influence exercises a monopoly over the world's base-metal industry in such manner as to exclude effective competition, and some allusion is made to the special case of steel hardeners. Some other trade openings are also briefly described, as the manufacture of volatile and essential oils, lubricants, perfumery, and drugs, and finally, an excellent summing-up of the whole question is provided. It is shown how Great Britain has been handicapped by unscrupulous German methods, by the insufficiency of our laws relating to patents and trade-marks, and by the protective tariffs of other countries, and stress is laid very sensibly and justly upon the legitimate factors of Germany's success. These include the willingness and ability of her people to work in co-operation and the financial backing of industrial enterprises by banks. Thus, it a German chemist has made a discovery which appears to be of commercial value, any of the large banks, on receiving a satisfactory report from their own scientist, will advance on favourable terms the capital necessary to run the business. Again, German businesses are conducted in such a way that there is never any difficulty in the subordinates obtaining access to those in command, who are always men of high technical skill and knowledge. The heads of businesses in Germany are always willing to work harder and longer hours than men of similar position in England, and they and their representatives are mostly men of linguistic ability. Our system of weights and measures and our neglect of modern languages are both serious bars to our foreign trade. Finally, Germany's wonderfully efficient system of education and her encouragement of research and the application of science to industry have contributed very materially to her success. The writer of the pamphlet clearly realises that we must waste no more time and energy on recapitulation and discussion of the causes of our failure; our task is now to make suggestions of remedies and act promptly upon those which appear to be efficacious. First and foremost he places the need for organisation, and some of his statements are well worth quoting; for example:—"The British race must make up its mind not to be beaten by the Germans either on the battlefield or in the markets, and to achieve this every individual must realise, as never before, that it is his duty to use all his abilities and his whole strength in order that he may contribute his full share to the improvement of the national welfare and the advancement of industry. . . . Conservative policies, whether in industrial or educational matters, must go by the board. Every well-planned attempt at improving industries or raising the standard of education should be practically supported. In business, as in education, much may be learned from Ger-

many without copying their shady methods. The British reputation for straight dealing must be preserved. As the commercial prosperity of Germany is largely due to superior scientific and technical training, knowledge of languages, and efficiency in trading methods, it is with these weapons that her trade must be attacked." He points out that Germany's weapons of attention to detail, skilful organisation of industries as a whole, superior technical training of employees and officials, &c., are "quite within the reach of our people; they have only to be taken in hand and utilised in a serious, systematic manner without delay."

How Belgium is Fed. Published by the National Committee for Relief in Belgium.

THIS pamphlet is slightly abridged from an interesting article, written by Mr. W. C. Edgar, and published a short time ago in the *North-Western Miller*, an influential American trade journal of which he is the editor and principal proprietor. Mr. Edgar, as a neutral, was able to visit Belgium to investigate for himself the work of the Commission for Relief. He took with him a gift from the American millers of food worth more than £120,000, for the distribution of which he made himself responsible. The accounts he writes of his visits to the kitchens, communal distribution places, &c., are most interesting, and the work done by the Commission may truly be described as affording an "amazing illustration of what can be accomplished by the genius of American business, joining with that of Belgium." The need for more money to carry on this great work is urgent, for destitution is bound to increase during the coming winter, and the outlook is very serious. The pamphlet contains a short article by John Galsworthy on the debt Britain owes to Belgium, and also the appeal of the National Committee for Relief in Belgium. From this latter the following may be quoted:—"All the neutral authorities on the spot are convinced that if the supplies of food to Belgium are discontinued the Germans will act up to their declaration that they will not, or cannot, save the seven million people from starving to death."

CORRESPONDENCE.

ESTIMATION OF SULPHUR IN GALENA.

To the Editor of the Chemical News.

SIR,—The following rapid method for the estimation of sulphur in galena may be of interest to some of your readers. It is very simple and can be carried out in less than an hour, and the results are excellent.

The method depends upon the precipitation of lead sulphate by the oxidation of the sulphur to sulphuric acid.

Weigh 1 grm. of the galena, together with about 1 grm. of potassium chlorate, and transfer to an eight ounce flask.

Treat the mixture with 10 cc. of concentrated nitric acid, place on a hot plate, and stir occasionally until the sulphur has dissolved.

When oxidation is complete, which should only take a few minutes, evaporate nearly to dryness and cool; add 50 cc. of water, and boil for a little while; remove from the hot plate, and allow the lead sulphate which is formed to settle.

Filter and wash by decantation several times; the residue is then transferred to a larger flask and dissolved in a strong solution of ammonium acetate; boil, and titrate with a standard solution of ammonium molybdate, using tannic acid as an indicator.

From the percentage of lead found the sulphur present can easily be calculated.—I am, &c.,

J. OWEN JOSEPH.

21, Brynshilf Terrace, Mount Pleasant,
Swansea, Sept. 8, 1915.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

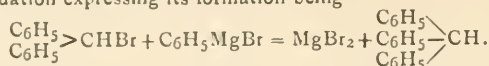
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxi. No. 5, August 2, 1915.

This number contains no chemical matter.

No. 6, August 9, 1915.

Preparation of Carbides of Formula $\text{C}_6\text{H}_5\text{C}\equiv\text{CH}-\text{R}$,

R being an Aromatic Nucleus.—F. Bodroux.—When an ethereal solution of bromo-diphenylmethane, $\text{C}_6\text{H}_5\text{CHBr.C}_6\text{H}_5$, is added drop by drop to an ethereal solution of phenylmagnesium bromide an energetic reaction occurs. When it is over the resulting liquid, after treatment with slightly acidified ice water, gives, on evaporation, an abundant white residue. The reactions of this compound show that it is triphenylmethane, the equation expressing its formation being—



The great reactivity of bromo-diphenylmethane is due to the fact that the bromine atom is attached to a carbon atom which is united with two electro-negative radicles. Bromo-diphenylmethane also undergoes double decomposition with the bromide of paratolyl magnesium, the product being paratolyl diphenylmethane. Bromo-diphenylmethane also reacts energetically with the bromide of α -naphthyl magnesium, and α -naphthyl diphenylmethane is formed, the yield being about 60 per cent.

Decomposition of β -Nataloin and of β -Homonataloin.—E. Léger.— β -Nataloin, obtained by the saponification of the inactive pentacetyl derivative, is always slightly active. This is due to the fact that crystallisation causes decomposition, as the following experiments show. A specimen of rotatory power -24° after three crystallisations in alcohol gave the value $\alpha_D = -145^\circ$; i.e., that of natural nataloin. A fourth crystallisation produced no further appreciable change in the rotation. The re-crystallisation of the mother-liquors of this laevo-rotatory aloin gave a dextro-rotatory aloin with $\alpha_D = +63^\circ$. This value could not be further increased, and it is probable that a compound is formed of d - and l -aloins, its rotatory power being that of a compound of five molecules of d -nataloin with two of l -nataloin. From β -homonataloin by three successive crystallisations a compound of rotatory power -147.6° was obtained, while the mother-liquor again gave a compound of five molecules of d - with two molecules of l -homonataloin rotatory power $+63^\circ$. Thus, both β -nataloin and β -homonataloin are racemic compounds which can be split up into the l -substances, identical with the natural products, and dextro-rotatory compounds of the composition given above.

MISCELLANEOUS.

British Association for the Advancement of Science.—The following were the Officers and Committee of Section B (Chemistry) at the Manchester Meeting of the British Association:—

President—Prof. W. A. Bone, D.Sc., F.R.S.

Vice-Presidents—Prof. W. J. Pope, M.A., LL.D., F.R.S.; Prof. W. P. Wynne, D.Sc., F.R.S.

Secretaries—A. Holt, D.Sc. (Recorder); C. H. Desch, D.Sc., Ph.D.; H. F. Coward, D.Sc.

Committee—E. F. Armstrong; E. C. C. Baly, F.R.S.; G. Baiger; P. Bedson; A. Borns; F. P. Burt; H. B. Dixon, F.R.S.; C. Dreyfus; C. A. Edwards; A. Findlay; G. J. Fowler; F. Francis; W. W. Haldane Gee; R. W. Gray; A. G. Vernon Harcourt, F.R.S.; A. Harden, F.R.S.; J. A. Harker, F.R.S.; P. Henry; E. Hope; J. Hübner; F. Jones; E. Knecht; A. Lapworth, F.R.S.; A. Liversidge; W. C. McC. Lewis; Sir H. Miers; H. N. Morris; J. E. Myers; K. J. P. Orton; R. H. Pickard; J. Ramsden; F. Ranwez; A. Ree; Sir T. K. Rose; W. Rosenhain, F.R.S.; Sir E. Rutherford, F.R.S.; H. J. S. Sand; N. V. Sidgwick; F. Soddy, F.R.S.; R. L. Taylor; W. Thomson; R. Threlfall, F.R.S.; Sir W. Tilden, F.R.S.; W. E. S. Turner; C. Weizmann; J. Wertheimer; H. Wooley; H. J. Yates; T. J. Young.

The Papers brought before the Section were as follows:—

Prof. W. A. BONE, F.R.S.—Presidential Address.

Dr. H. F. COWARD and Prof. A. HARDEN—Description and Exhibition of Diagrams used by Dalton in illustrating his Atomic Theory.

Prof. P. HENRY—Vinyl Acetic Nitrile.

Dr. H. J. S. SAND—Experimental Demonstration of New Cadmium Vapour Electric Arc Lamp.

Reports of Research Committees:—

(a) Hydro-aromatic Substances.

(b) Transformation of Aromatic Nitro-amines.

(c) Dynamic Isomerism.

(d) Plant Enzymes.

(e) Solubility Phenomena.

(f) Crystalline Form and Molecular Structure.

(g) Natural Plant Products of Victoria.

(h) Influence of Weather Conditions on the Amount of Nitrogen Acids in Rainfall and the Atmosphere.

(i) Non-aromatic Diazonium Salts.

(j) Utilisation of Brown Coal By-products.

(k) Botanical and Chemical Characters of the Eucalypts.

Discussion on Radio-active Elements and the Periodic Law, opener Prof. F. SODDY, F.R.S.

Papers on Flame and Combustion, with experimental Illustrations:—

(a) Prof. H. B. DIXON—The Explosion of Gases.

(b) Dr. H. F. COWARD—The Dilution Limits of Inflammability of Mixed Inflammable Gases with Air.

(c) Prof. W. A. BONE—Gaseous Combustion at High Pressures.

Papers on Smoke and its Prevention:—

(a) E. D. SIMON—Lines of Research in Smoke Abatement.

(b) W. W. HALDANE GEE—Manchester and the Smoke Problem.

(c) Prof. KNECHT—Some Constituents of Manchester Soot.

(d) Prof. WYNNE—Atmospheric Pollution.

(e) H. J. YATES.

(f) V. HARCOURT—Smoke Prevention in Domestic Grates.

(g) Prof. W. A. BONE—The Bone-Callendar-Yates Bolometer.

(h) Prof. RANWEZ—Damage caused to Vegetation by Smoke and Vapours.

(i) A. G. RUSTON—Reasons for Smoke Damage to Plants.

(j) W. W. HALDANE GEE—Electrical Precipitation of Smoke.

Prof. W. J. POPE, F.R.S.—Experimental Demonstration of Liquid Crystals.

Papers on Homogeneous Catalysis—Prof. W. C. McC. LEWIS; J. RICE; Prof. F. FRANCIS; N. V. SIDGWICK; Prof. E. C. BALY.

W. E. S. TURNER—Ionisation in Solvents of Low Dielectric Constant.

W. E. S. TURNER and J. D. CAUWOOD—The Molecular State of Salts in Solution.

THE CHEMICAL NEWS.

VOL. CXII., No. 2913.

THE CADMIUM-VAPOUR ARC-LAMP.*

By Dr. H. J. S. SAND.

THE cadmium-vapour arc lamp exhibited, the use of which is recommended for polarimetric and other purposes, is comparable in general principle with the well known mercury vapour lamp. The lamp is constructed of quartz-glass, and the cadmium is freed from oxide and dissolved gas by a process of filtration while at the pump. It is hindered from adhering to the glass by the presence of a small amount of a loose powder (zirconia) in the lamp. The metal is melted by external heating before starting, and maintains itself in the molten condition by the heat of the current. Once started the lamp may be kept burning for an indefinite time.

EXAMINATION AND ESTIMATION OF THE DAMAGE CAUSED TO VEGETATION BY THE SMOKE AND VAPOURS FROM FACTORIES.*

By Prof. FERNAND RANWEZ, University of Louvain.

VERY many works and factories emit smoke so abundantly as to cause harm to vegetation. Some of them also emit gases which are noxious to plants, and so blight the neighbouring country.

When the fumes are very pronounced the destructive effects are clearly seen, as, for example, near those works which pour out large quantities of sulphur dioxide. In the immediate neighbourhood of such works the plants exposed to the frequent action of the gas have their leaves scorched, while trees lose their leaves and show many dead branches, the action of the gas gradually killing them entirely.

Though these are the most acute symptoms there are many others far less pronounced, every intermediate condition being observable between plants which exhibit only a slightly checked development and those which die from evident poisoning. Factory smoke and the damage it produces raise frequent complaints from neighbouring landowners and farmers, who are or believe themselves to be injured, and consequently the courts and experts have to decide the following questions:—1. Has the land of such a person suffered damage, and if so to what extent? 2. Is the damage wholly or in part the result of the smoke from the factories complained of? The solution of these questions necessitates a comparative study of the general conditions of cultivation and an examination of the actual smoke deposits both on the damaged lands near the works which emit the noxious vapours and districts various distances away.

If perhaps the scorched leaves exhibit some characteristic aspect there may exist some cause other than mere smoke capable of producing such damage.

The damage is often limited to diminished growth and spread of vegetation, or to a slow withering, and many causes besides smoke produce these effects, such, for example, as faulty cultivation and sour or poor soil.

Vapours often leave their imprint, as, for example, sulphur dioxide (one of the commonest destructive agents), which can be recognised in plants in the form of sulphate. But plants usually contain sulphates in very varying proportion even without the direct action of the gas, so it

follows that the discovery of more or less characteristic forms of damage, the observation of the diminution of the spread and growth of plants, or their destruction, the presence of an increased quantity of sulphates or other compounds which could have arisen from vapours, do not sufficiently prove the destructive effects of gas when they are considered by themselves alone without all contingent circumstances. The observations only yield proof when they are contrasted with similar ones taken with due care on plants of neighbouring districts. To make such comparative experiments one must describe round the offending factory a series of concentric circles of ever-increasing radius, and then see (1) whether in the more distant regions the vegetation presents normal features, (2) whether it exhibits abnormalities on approach to the factory, and (3) whether such abnormal features become proportionately more marked as the plants become more exposed to the action of the gas.

In all such observations account must be taken of the general cultural conditions of the compared areas. Mere distance from the point of origin is not, however, the only factor on which the noxious action of such vapours depend, for many other factors come into play, such as the prevalence of wind, humidity of the atmosphere, &c.

PRELIMINARY OBSERVATIONS ON THE NITRILE OF VINYLACETIC ACID.*

By Prof. PAUL HENRY, University of Louvain.

SEVERAL methods have been tried to prepare the substance $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CN}$. One might mention the action of moist KCN on allyl iodide, which gives by a molecular transformation the nitrile of crotonic acid $\text{CH}_3-\text{CH}=\text{CH}-\text{CN}$, and also the action of solid KOH on the nitrile of chlorbutyric acid $\text{CH}_2\text{Cl}-\text{CH}_2-\text{CH}_2-\text{CN}$, which, however, yields a trimethylene derivative—



It is believed that the nitrile of vinylacetic acid has been prepared by heating for several hours at a temperature of about 120° C. a mixture of $\text{C}_3\text{H}_5\text{I}$ and anhydrous $\text{Cu}_2(\text{CN})_2$, when a product is obtained which boils at 118° C. and has no smell of an isonitrile derivative.

In order to identify the substance thus obtained, the oxidising action of a cold neutral solution of KMnO_4 was first tried. Malonic acid, which should be the characteristic oxidation product of this nitrile, was not definitely obtained, probably because oxidation had proceeded too far.

The action of organo-magnesium compounds to give acetones ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{CO}-\text{R}$) was also unsuccessful, for the substances BrMgC_2H_5 and BrMgC_6H_5 only yielded resinous bodies. The action of ozone was next examined. The ozonide of crotonic nitrile when treated with water gave acetaldehyde, but the syrupy ozonide obtained from vinylacetic nitrile was found on analysis to possess the composition anticipated, and when treated with water yielded no acetaldehyde. Its decomposition products have been examined.

IONISATION IN SOLVENTS OF LOW DIELECTRIC CONSTANT.*

By W. E. S. TURNER.

IN extension of previous work on conductivity in solvents of low dielectric constant, Sachanov has found that the conductivity of a mixture of electrolytes exceeds that of the sum of the conductivities of the single electrolytes by

* Read before the British Association (Section B), Manchester Meeting, 1915.

* Read before the British Association (Section B), Manchester Meeting, 1915.

an amount which is greater the lower the dielectric constant of the solvent (*Zeit. Phys. Chem.*, 1914, lxxxvii., 441). From his results he argues that in solvents of the type used the degree of dissociation of one electrolyte is materially increased by a second one added.

This interpretation is capable of test by freezing or boiling-point tests on the solutions. Experiments on solutions in chloroform, one of the solvents used by Sachanov, show that the salts tetrapropylammonium iodide, diethylammonium chloride, triethylammonium bromide, phenylethyl and phenyldiethylammonium chloride and iodide, so far from causing increased dissociation when dissolved in pairs, have just the reverse effect, producing an increased degree of association; that is to say, Sachanov's interpretation is incorrect, and whereas in water the molecular conductivity increases as the average size of the electrolyte molecules decreases, in solvents of low dielectric constant the reverse is the case.

This conclusion is in harmony with several phenomena previously pointed out by the writer (*Trans. Chem. Soc.*, 1911, xcix., 880), and also with the fact that the conductivity in solvents of low dielectric constant increases as the molecular size of the solute increases.

THE MOLECULAR STATE OF SALTS IN SOLUTION.*

By W. E. S. TURNER and J. D. CAUWOOD.

At the 1910 meeting of the Association one of us demonstrated that the haloid salts of organic ammonium, sulphonium, and oxonium bases were highly associated in a neutral solvent—*e.g.*, chloroform—and evidence was tendered to prove that salts in general are complex molecular substances. Subsequent investigations have brought within the scope of these conclusions metallic salts, whilst the effect of the solvent has also been thoroughly tested. As the salts hitherto employed have been the haloid salts almost entirely, the general conclusions would be greatly strengthened if it could be shown that salts of acids other than the haloids are also associated.

For the purpose of this investigation, therefore, a number of new salts have been prepared, including tetrapropylammonium fluoride, chlorate, bromate, iodate, sulphate, thiocyanate, oxalate, and benzoate. All of them have high molecular weights in chloroform. Thus, the observed molecular weight of the thiocyanate in 4 per cent solution is nearly seven times the value for the simple formula.

At the same concentration (25 mgrms. molecule per 100 cc. of solvent) the degree of association increases in the order: iodate, oxalate, chloride, bromide, bromate, chlorate, sulphate, iodide, benzoate, nitrate, periodide, thiocyanate, fluoride.

DYNAMIC ISOMERISM.†

a'-Chlorocamphor.‡

DURING the past year the principle of dynamic isomerism has been applied in preparing, in a pure state and in considerable quantity, the first member of a hitherto unisolated series of halogen derivatives of camphor. *a*-Chlorocamphor, as Kipping found in 1905, becomes

isodynamic with the stereoisomeric *a'*-chlorocamphor when alkali is present; when the alkali is removed the isomerism again becomes static, and the isomerides can be separated by ordinary methods of fractionation.

a'-Chlorocamphor presents several points of special interest:—

First. It lies on the borderland between the more labile and the wholly stable forms of isomerism; if proper precautions are taken the *a'*-compound can be kept an indefinite time, but if carelessly handled (*e.g.*, if crystallised from a medium containing traces of alkali) it may at any time revert to the less soluble and therefore more stable *a*-compound.

Second. When brominated it gives a mixture of stereoisomeric *aa'*-bromochlorocamphors in exactly the same proportions as when *a*-chlorocamphor is brominated, *i.e.*, the position taken up by the bromine is not affected in the least by the position which the chlorine atom occupies. This remarkable result is in agreement with Lapworth's view, that in the bromination of ketones it is an enolic isomeride that is first attacked; more generally we may conclude that at some stage in the bromination *a*- and *a'*-chlorocamphor give rise to some identical intermediate product.

Third. In complete contrast with their behaviour on bromination, *a*- and *a'*-chlorocamphor give on nitration the pure chloronitrocamphor directly derived from the chlorocamphor employed; thus *a*-chlorocamphor gives *a*-chloro-*a'*-nitrocamphor, whilst *a'*-chlorocamphor gives an excellent yield of *a'*-chloro-*a*-nitrocamphor. The latter compound has already been fractionated out in small quantities from the mixture of stereoisomers which is obtained by chlorinating *a'*-nitrocamphor, but as *a'*-chlorocamphor can be prepared and nitrated on a large scale, the nitro-derivative will now be available in much larger quantities. This fact may be of considerable importance, since the reduction of the chloronitro-compound may give the long-sought but still unknown *a*-nitrocamphor.

Fourth. *a'*-Chlorocamphor appears to lose hydrogen chloride much more readily than the *a*-compound. If this decomposition should involve the removal of a hydrogen atom from the nucleus an entirely new chapter in the chemistry of camphor may be begun.

In view of the large amount of work that is waiting to be done in this and in other directions the Committee asks to be reappointed, with a grant sufficient to defray the cost of extending the experiments to the β and π derivatives of camphor.

THE TRANSFORMATION OF AROMATIC NITRO-AMINES AND ALLIED SUBSTANCES AND ITS RELATION TO SUBSTITUTION IN BENZENE DERIVATIVES.*

VERY little work has been possible in the circumstances throughout the year owing to preoccupation with other more pressing duties, and to the departure for military and other like services of the senior students, who would have carried out the experimental part of the investigation. The work, of which a short report follows, is therefore to be regarded as purely of a preliminary character.

The Relation of the Velocity of Chlorination of Aromatic Compounds to Constitution.

(With D. C. JONES.)

The measurement of the velocity of chlorination of a number of acylanilides, acylchloroanilides, and acyltoluidides, and acylxyliides (Orton and King, Reports, 1911;

* Read before the British Association (Section B), Manchester Meeting, 1915.

† Report of the Committee, consisting of Prof. H. E. Armstrong (Chairman), Dr. T. M. Lowry (Secretary), Prof. Sydney Young, Dr. C. H. Desch, Sir J. J. Dobbie, and Dr. M. O. Forster (Drawn up by the Secretary). Read before the British Association (Section B), Manchester Meeting, 1915.

‡ The experiments on *a'*-chlorocamphor have been made by Mr. Victor Steele, and are described in detail in a joint paper recently communicated to the Chemical Society.

* Report of the Committee, consisting of Prof. F. S. Kipping (Chairman), Prof. K. J. P. Orton (Secretary), Dr. S. Ruhemann, and Dr. J. T. Hewitt. Read before the British Association (Section B), Manchester Meeting, 1915.

Trans. Chem. Soc., 1911, xcix., 1377) showed that the velocity of the reaction was highly sensitive to:—

- (a) The nature of the acyl group;
- (b) The nature of a substituting group, chlorine or alkyl, present in the substance;
- (c) The position of the substituting group.

It has been our intention to extend these observations by studying the influence of substituents other than chlorine and alkyl, for example, bromine and the nitro-group, and to compare with the amino- and the acylamino-group, —NHAc, such other ortho-para-directing groups as hydroxyl-, alkoxy-, and alkyl.

It is hoped that by study of a number of substances of suitable constitution the relative activities of directing groups in chlorination might be expressed as numerical values. The investigation is not of the simplest, for direct measurement in the case of an aniline or phenol, and so forth, is rarely possible owing to the very great speed of entrance of the first and often further chlorine atoms. Derivatives in which other groups, such as the nitro-group, are present must be used in order to obtain a measurable rate of chlorination. Holleman has in recent years made attempts to compare the activities of directing groups by nitrating compounds which contain two directing groups and then estimating the proportion of the different nitro-derivatives in the product. By this means he has arrived at certain relations, which can be expressed numerically. Our method has the advantage of being simpler in manipulation, and should at least yield more direct values.

Experimental Method.—The method of experiment has now been thoroughly tested and has not been modified in these later experiments (Orton and Jones, Reports, 1910; Orton and King, *loc. cit.*).

(1) *The Effect of the Nitro-group.* A nitro-group in the para position with respect to the directing group greatly inhibits chlorination; the effect is still more marked when the nitro-group is in the ortho-position. In the case of phenols the nitro-group appears to have some definite specific action; phenols are chlorinated with very great speed, but chlorination of *o*- and *p*-nitrophenols, especially of the former, is very slow. *o*- and *p*-nitroaniline, on the other hand, are chlorinated at speeds which differ little from those observed with the corresponding monochloroanilines. Although the amino-group is a far more active directing group in chlorination than the hydroxy-group, this result would indicate that a free hydroxy-group is not present in *o*- and *p*-nitrophenol.

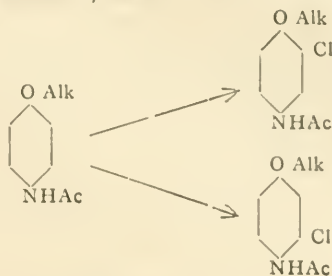
(2) *Alkoxy-groups as Directing Groups in Chlorination.*—Measurements have shown that the methoxy- and ethoxy-groups have a quite unexpectedly high activity in chlorination. The entrance of the first chlorine atom into anisole, $C_6H_5.OCH_3$, and into phenetole, $C_6H_5.OC_2H_5$, is "instantaneous." The values of the velocity coefficients, k_{11} , for the second chlorine atom, together with those of the corresponding phenols, are given in the table:—

	k_{11}		k_{11}
<i>o</i> -Chlorophenol ..	57	Chloroanisole ..	1.5
<i>p</i> -Chlorophenol ..	32	Chlorophenetole ..	3.0
Acetanilide ..	40	<i>p</i> -Chloroacetanilide	0.2

The alkoxy-groups are less active than the hydroxy-groups, but their value is brought out by a comparison with acetanilide and *p*-chloroacetanilide. For acetanilide k_{11} is 40, whilst for anisole and phenetole it is too rapid for measurement ("instantaneous"), that is, over 1000, and for *p*-chloroacetanilide the value is 0.2 as compared with 1.5 or 3.0 for the ethers.

This high activity of the methoxy- and ethoxy-groups accounts for the high values observed by us in the chlorination of acetoaniside ($k_{11}=60$) and acetophenetide ($k_{11}=90$) (Orton and King, *loc. cit.*), in each of which are two directing groups, alkoxy- and acetamino-. Moreover, the products of the chlorination should in these compounds be a mixture in which the chloro-compound

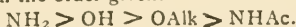
formed under the influence of the alkoxy-group would largely predominate; thus:—



As nothing at the time was known of the activity of the alkoxy-groups in directing substitution, we (Orton and King, *loc. cit.*) took the monochlorophenetide, which we isolated only by repeated crystallisation of the first product, to be 5-chloroacetphenetide. The relatively greater activity of the ethoxy-group would indicate that the chloro-derivative in larger proportion is the isomeric 2-chloroacetphenetide. Prof. J. F. Thorpe has, moreover, recently prepared the 5-chloroacetphenetide and demonstrated its constitution undoubtedly, and has further shown that the compound which we isolated is 2-chloroacetphenetide.

(3) *A Comparison of the Amino- and Hydroxy-groups.*—A direct comparison between the amino- and hydroxy-groups in their activities in directing chlorination is not very easy to obtain; the speeds of entrance of the first and second atoms of chlorine into aniline and phenol are very high; the introduction of the nitro-group, which lowers the speed of chlorination, is not permissible owing to its specific effect, mentioned in the foregoing, on the hydroxy-group. Moreover, a further difficulty in obtaining an exact relation arises from the great difference in the activities of the two groups. The most trustworthy method is found in the measurement of the rate of entrance of the third chlorine atom into 2:4-dichloroaniline and 2:4-dichlorophenol respectively. The value of k_{11} 18.4° for the aniline is about 600 and that for the phenol approximately 0.16.

Summary.—The amino-group far surpasses all other groups in activity in chlorination of aromatic compounds, and is followed by the groups, hydroxy-, alkoxy-, and acetamino- in the order given.



The Committee ask for reappointment, and for a grant of £10 for the year 1915-16.

RESEARCH ON NON-AROMATIC DIAZONIUM SALTS.*

2-AMINOTHIAZOLE, produced by the condensation of thio-carbamide and chloro-acetaldehyde alcoholate, is a non-aromatic base exhibiting a certain degree of diazotisability. It was formerly known that in concentrated hydrochloric or hydrobromic acid the base reacted with nitrous acid to yield a very unstable diazo-derivative, not hitherto isolated from solution. This unstable product speedily lost its diazo-nitrogen, giving rise to 2-chlorothiazole or 2-bromothiazole. In feebly acid solution the diazotisation of 2-aminothiazole was known to yield an ill-defined sparingly soluble thiazole-2-diazo-hydroxide.

(With G. V. MONOW, Ph.D., A.R.C.Sc.1.)

The foregoing observations on the instability of the diazo-derivatives of 2-aminothiazole in the presence of

* Interim Report of the Committee, consisting of Dr. F. D. Chattaway (Chairman), Prof. G. Morgan (Secretary), Mr. P. G. W. Bayly, and Dr. N. V. Sidgwick. Read before the British Association (Section B), Manchester Meeting, 1915.

The permanganate used in the first three was of such strength that 1 cc.=0.00318 grm. $\text{Na}_2\text{C}_2\text{O}_4$ or

0.000680 grm. $K_2C_4H_4O_6\frac{1}{2}H_2O$, while in the last two
I cc. = 0.00676 grm. $Na_2C_2O_4$, or 0.00142 $K_2C_4H_4O_6\frac{1}{2}H_2O$.
This work was done at the suggestion of Prof. V. H.
Gottschalk.

Laboratory of the Missouri School of Mines,
Rolla, Mo.

THE ANALYSIS OF PLATINUM.*

By F. MYLIUS and A. MAZZUCHELLI.

(Concluded from p. 146).

CASE B.—INVESTIGATION OF NOMINALLY PURE PLATINUM.

In order to determine the small impurities in nominally pure platinum and to establish its degree of purity, the metal (e.g. 50 grms.) is dissolved as impure platinum and converted into the sodium double chloride by the addition of pure sodium chloride; this is then repeatedly recrystallised from 1 per cent aqueous solution (cf. Mylius and Foerster, *loc. cit.*). After 95 to 99 per cent of the platinum has thus been removed as double chloride, purified and freed from adulterations, the foreign metals are contained in the mother-liquor, rich in sodium chloride if they have not remained behind as precipitates on the filters used for the clearing of the alkaline salt solution. The acid solution of these precipitates is added to the (usually brown) mother-liquor, which is first evaporated to dryness with aqua regia and hydrochloric acid; it is then heated to 150°, so that the residue consists of impure sodium platinum chloride with sodium chloride. On treatment with water silicic acid, gold, silver chloride, &c., may remain behind and be filtered off.

The impure chloride solution may now be investigated as in Case A, the impurities being first summarily separated from the platinum by the hypochlorite method; but owing to the large amount of sodium chloride the following method can also be employed.

The aqueous solution is made a little acid, and then ammonium chloride solution is added till a fresh addition of it produces no appreciable precipitate. The platinum ammonium chloride (precipitate I.) which is now filtered off contains only a little iridium, which will be taken into account later.

By treating the filtrate for hours in the warmth with sulphuretted hydrogen the small residue of platinum is precipitated together with all the precipitable impurities (except those of the iron group). If lead or volatile metals are present the precipitate must be dissolved in dilute aqua regia; otherwise it is more convenient to ignite the washed sulphide in the air and dissolve the product of ignition in aqua regia. (Insoluble metal is to be regarded as iridium, &c.). The filtered chloride solution is now treated as explained in the above description (Nos. I.—II.) of the isolation of the individual impurities—i.e., it is precipitated successively with ammonium chloride, sulphuretted hydrogen, &c. Iron, nickel, cobalt, &c., must be sought for in the solution containing sodium chloride, which has been freed from the platinum metals by H_2S .

Special care must be used in the determination of iridium, for otherwise this very usual impurity may escape detection in the presence of much platinum.

In the method of analysis described here ammonium chloride, on account of the errors it is known to cause, is used as little as possible in the determination of platinum, but it cannot be altogether dispensed with.

Any iridium must be removed from all the platinum ammonium chloride precipitates with which it has been precipitated (especially in precipitation I.). For this purpose hydrazine can conveniently be used, for it precipitates the platinum as metal in strong hydrochloric acid

solution while the iridium remains in the acid mother-liquor.

By the process described above, which takes into account only the commonest impurities, and cannot therefore be regarded as exhaustive, the analytical examination of platinum metal which is supposed to be pure is attended with difficulties which can be surmounted only by using special care. A part of the difficulty which is not so easily overcome consists in the recognition every time of the numerous impurities of a rarer kind which may be present in traces in the platinum, either as metal or not.

Larger quantities of impurities can be determined with sufficient accuracy, but as the purity of the platinum metal increases the method of determining its degree of purity loses its reliability very much. The detection of $\frac{1}{100}$ per cent of total impurity can be carried out with certainty by the method recommended (fourth degree of purity). The analytical characterisation of a platinum material of the fifth degree of purity (total impurity is to the platinum as 1 : 10⁵) is, however, hardly possible with certainty.

IV. RESULTS OF ANALYSES AND EXAMPLES.

1. 2 grms. of nominally pure platinum were dissolved with 0.2 grm. of iridium, and with 0.2 grm. each of Pd, Au, Rh, Cu, and Fe. The approximate analysis gave:—

	Present.	Found.
Iridium ..	1.0 per cent	1.17 per cent
Palladium ..	0.1 "	0.08 "
Rhodium ..	0.1 "	0.08 "
Copper ..	0.1 "	0.10 "
Iron ..	0.1 "	0.098 "
Gold ..	0.1 "	0.12 "

2. 5 grms. of platinum were dissolved with 0.025 grm. of iridium and 0.005 grm. of each of the other metals. The proximate analysis gave:—

	Present.	Found.
Iridium ..	0.50 per cent	0.70 per cent
Palladium ..	0.10 "	0.074 "
Rhodium ..	0.10 "	0.080 "
Copper ..	0.10 "	0.096 "
Iron ..	0.10 "	0.092 "
Gold ..	0.10 "	0.070 "

3. 1 grm. of platinum was dissolved with 0.003 grm. of each of the seven foreign metals. The proximate analysis gave:—

	Present.	Found.
Iridium ..	0.0030 grm.	0.0042 grm.
Palladium ..	0.0030 "	0.0023 "
Rhodium ..	0.0030 "	0.0020 "
Copper ..	0.0030 "	0.0030 "
Iron ..	0.0030 "	0.0027 "
Gold ..	0.0030 "	0.0018 "
Silver ..	0.0030 "	0.0028 "
	0.021 "	0.0188 "

0.0022 grm., or 0.22 per cent of the alloy, was lost.

4. 1 grm. of natural platinum ore in grains. The part soluble in aqua regia (about 3.5 per cent osmiridium, &c., insoluble):—

Platinum ..	78.5 per cent
Iridium ..	4.0 "
Rhodium ..	0.2 "
Palladium ..	0.1 "
Gold ..	0.2 "
Iron ..	13.6 "
Copper ..	2.6 "
Nickel ..	0.6 "
Cobalt ..	" "
Silver ..	Trace

* Zeitschrift für Analytische Chemie, lxxxix., 1.

5. Muffle of commercial platinum regarded as good in technics.

Approximate analysis of the other constituents in 10 grms. :—

	I.	II.
Iridium	2.2 per cent	2.23 per cent
Palladium .. .	?	0.13 "
Gold	0.30 "	0.3 "
Rhodium .. .	Trace	Trace
Copper	0.13 "	0.18 "
Iron	0.13 "	0.12 "
Nickel, &c. ..	Trace	Trace
	about 3.0 "	2.96 "

6. Muffle of commercial platinum, much corroded with formation of soot.

Approximate analysis of the other constituents in 10 grms. :—

Iridium	1.61 per cent.
Palladium .. .	0.15 "
Gold	—
Rhodium .. .	0.15 "
Copper	0.09 "
Iron	0.11 "
Silver	Trace
Nickel	"
Undetermined ..	0.1 "
	2.25 "

7. Nominally pure platinum. Foil freed from iron by HCl by Heraeus. 20 grms. gave on analysis according to method above, traces of iridium, palladium, gold, copper, and iron to a total amount of about 0.01 per cent. The material would thus belong to the fourth degree of purity ($1:10^4$).

V. RESULT OF THE INVESTIGATION.

The scope of platinum analysis is so wide that it is not easy to make it exhaustive. In particular the chapter "Small Impurities" shows the extent and the need for care in the investigations.

Our work is only a limited contribution to it, for it relates exclusively to the ordinary constituents of platinum ores and neglects the rarer ones.

The result of our work may be summarised in the following statements :—

1. The qualitative reactions carried out with gramme-litre solutions of the platinum metals are brought together and compared.

2. The method of performing colorimetric determinations with hydrochloric acid chloride solutions are shortly described.

3. A simple process for the analysis by precipitation of dissolved platinum alloys is recommended.

4. The behaviour of ruthenium chloride towards ammonium chloride is explained by means of new experiments.

5. The existence of iridium mercaptide is proved.

6. Methods of separating platinum metals from one another are tested and improved.

7. A special method is proposed and described in detail for the quantitative analysis of technical platinum.

8. For the analytical detection of impurities in nominally "pure" platinum a method is described as a supplement to that recommended by Finkener and tested by Mylius and Perster for the purification of the metal.

LEATHER INVESTIGATIONS.*

THE COMPOSITION OF SOME SOLE LEATHERS.

By F. P. VEITCH and J. S. ROGERS.

Composition of Normal Sole Leather.

VEGETABLE-TANNED leather is essentially a compound or mixture of hide or fibrous proteid material with tannin. Depending on the use to which it is to be put, it may be finished in several ways whereby the composition of the final product may differ greatly from the simple compound. The tanned leather may be used without material change in composition, as for shoe soles; it may be greased, as for harness and belting; or it may be greased and dyed, as for harness and shoe uppers.

In addition to the insoluble hide and tannin which are the essential constituents of leather, moisture, mineral matter, fats, and water-soluble tanning materials, which remain to a small extent in well-scoured leather, are present. All of these, when not present in excessive quantities, are proper and normal constituents of the leather. In fact, the presence of a large percentage of oils or fats, even in sole leather, is of decided advantage in increasing the water resistance, flexibility, softness, and life of the leather, while the presence of a small amount of uncombined tannin is often of some advantage in retarding water penetration and hardening of the leather and in making it solid and firm. The presence of a large excess of uncombined tannin materials other than those mentioned is useless or harmful.

Leather is not a definite compound and is therefore impossible to produce of an exact composition. The ratio of combined tannins to hide substances approximates 7 to 10, while the percentages of water-soluble constituents, mineral matter, fat, and moisture may vary considerably. Careful study of the analyses of well-tanned scoured leathers of various tannages, both American and foreign, warrants the conclusion that well-tanned merchantable scoured sole leather of all tannages on analysis should give results on a moisture-free basis which fall between the following limits :—Leather substance from 75 to 93 per cent, hide substance from 43 to 57 per cent, combined tannins from 31 to 42 per cent, water-soluble materials from 5 to 15 per cent, oils and fats from 1 to 6 per cent, ash from 0.25 to 1 per cent.

Well-tanned honestly-made leather should approach the upper rather than the lower limits for leather substance and oils and fats. The water-soluble constituents should consist only of the materials contained in the adhering tannin solution which have not been removed in scouring.

Properly air-dried sole leather should not contain, even in very damp weather, more than 20 per cent of moisture, and the average percentages for the year should fall below 15 per cent. Neither the ultimate buyer nor the shoe manufacturer should be called upon to pay for a greater average amount than this. It will be observed that the leathers reported herewith contain much less moisture, due largely to the fact that they dried out very much after reaching the laboratory.

Normal vegetable-tanned sole and harness leather when burned should not leave more than 1 per cent of ash and as a rule not more than 0.5 per cent. This ash is derived from the hide, from the lime used in unhairing, and from the salts usually dissolved in all waters. The magnesia of the ash when calculated to Epsom salts, $\text{MgSO}_4 + 7\text{H}_2\text{O}$, the form present in air-dried leather, should not exceed 1 per cent.

It is customary abroad to consider less than 2 per cent of glucose permissible, the assumption being that this amount may be present from the tanning materials. It is very doubtful if this amount of glucose is ever present in normal leathers from which the excess of tanning materials has been properly washed. Leathers on which the final

* Bulletin No. 165, U.S. Department of Agriculture, Bureau of Chemistry.

liquors were sweet and exceptionally concentrated, and which are subsequently washed but little, may contain between 1 and 2 per cent of sugars, determined as dextrose.

The ether extract or fat may be as high as 5 per cent, probably never much less, to give pliability, water resistance, and durability to the leather.

Weighting of Leather.

During an extended examination of sole leathers now in progress, it has been found that a surprisingly large percentage contains great quantities of foreign materials. Although it has long been known that some tanners make a practice of weighting or loading their leather, the extent of the practice is not appreciated outside the tanning and closely related industries. Tanners state that leather is loaded with foreign materials because the boot and shoe makers will buy only the lower priced leather, which, to use a trade expression, "cuts to advantage"; that is, from which the greatest number of soles can be cut at the lowest cost a pair. Many boot and shoe manufacturers claim that they use loaded leather because it cuts to better advantage than the same leather not loaded.

The character, value, and wearing quality of leather varies with the part of the skin from which it is made. The skin from the upper part of the body and along the back is closer fibered than that from the lower part, under the body; it becomes more open textured, and consequently more porous as it passes from the backbone to the under side of the body. The skin over the posterior portion of the body is of closer texture than that over the forequarters; consequently the best leather is made from the hide in the region of the kidneys and hips, provided the skin is sound and not damaged in tanning. The leather from the "flanks" and "bellies" is more porous, lighter, and more flexible than that made from the "back," and in cutting the side of leather into soles the lighter and more flabby the lower portions the more of it is rejected. If, however, this lower portion has been stiffened and weighted with foreign material, no matter how useless it is nor how soon it may wash out, some shoe manufacturers will cut it into soles, thus obtaining more soles from a side. Because of these facts the shoe manufacturers calculate that weighted leather costs them less for each pair of soles than the unweighted leather.

Unloaded flabby leather makes poor shoe soles, and loading with materials readily soluble in water, as glucose and Epsom salts, increases the cost to the purchaser and does not make soles more serviceable.

Weighting Materials and their Effects.—Loading or weighting materials are cheap. Those in most general use in this country are glucose, selling at 2 cents a pound, Epsom salts, or magnesium sulphate, selling at 1 cent a pound, and solutions of tanning or other organic materials, selling at 0.75 to 2 cents a pound. Barium sulphate and lead sulphate—generally formed by drumming the leather first in a solution of barium chloride, costing 2 cents a pound, or of sugar of lead at 9 cents a pound, and then in sulphuric acid—and sodium sulphate, costing 1 cent a pound, are also employed to a small extent. Of these loading materials, glucose, soluble organic materials containing little or no tannin, magnesium sulphate, barium sulphate, lead sulphate, and sodium sulphate are much more objectionable than a small excess of actual tanning material.

Loading with glucose, Epsom salts, barium sulphate, lead sulphate, excessive quantities of tanning materials, or with water-soluble organic material is often detrimental to leather. It is made hard, brittle, more likely to crack, and after the loading washes out, as usually happens quite readily except in the case of barium and lead sulphates, it is more easily penetrated by water. Loaded leathers are more expensive, less durable, and a menace to health. A distinction should possibly be made between the effects of an excess of true tannin and of other uncombined or loading materials. The excess of true tannin may not

itself be so objectionable, and may even be of temporary advantage, because the slowly soluble tannins make the leather more water resistant, and impede the removal of combined tannin from the leather.

Quantity of added Weighting Materials.—The amounts of materials found in the loaded leathers examined are summarised as follows:—Ash, from 0.2 to 2.7 per cent; ether extract, from 0.4 to 5.6 per cent; Epsom salts, from 0.2 to 7.5 per cent; glucose, from 0.2 to 12.4 per cent; water-soluble materials, from 13.4 to 34.3 per cent; water-soluble tannin, from 6.1 to 17.8 per cent.

If it is feasible to secure the lower figures, as it appears to be in a number of tanneries, the higher figures must represent very excessive quantities. A comparison of these with the figures given for normal leathers shows that the percentages of ash, Epsom salts, glucose, and water-soluble materials are, as a rule, above the permissible quantities, while the amounts of fats and oils and actual leather substance are lower than they should be. These figures show a serious moral, economic, and business condition. Approximately, 63 per cent of the leathers examined are weighted with glucose, Epsom salts, or both. This loading varies from 1 to 7.5, with an average of 3.1 per cent of Epsom salts, and up to 10.4, with an average of 5.5, per cent of glucose, and amounts to a total maximum loading, when both are present, of 16 per cent and an average of 8 per cent.

Waste of Materials in Weighting Sole Leather.—The tanners whose leathers have been examined produce a large percentage of the sole leather made in this country. It seems probable, therefore, that these samples are fairly representative of American sole leather, and if this be true fully 60 per cent of the sole leather is loaded with Epsom salts or glucose, or both, and practically all of it contains more uncombined tanning materials than it should.

If 60 per cent of the sole leather contains an average of 8 per cent of Epsom salts and glucose, at least 150,000,000 pounds have been weighted annually with no improvement in its wearing value. The people have paid for not less than 12,000,000 pounds of Epsom salts and glucose, plus a profit to the tanner for working them into the leather, and have obtained nothing of value thereby. The average amount of water-soluble material in these sole leathers is 23 per cent. Subtracting from this the average percentage of glucose and Epsom salts found gives the percentage of what for brevity may be called "uncombined tanning" materials, meaning the materials derived from the tanning liquors in which the leather was tanned.

The almost universal practice of weighting or loading with excessive quantities of uncombined tanning materials is perhaps the most reprehensible form of weighting. It is needless, and wastes valuable materials which can be employed in the production of more leather, and it often leads to bleaching or addition of glucose or Epsom salts to conceal the injury which frequently results from the presence of excessive quantities of uncombined tanning materials. The elimination of this waste would not only conserve our fast-diminishing native tanning materials, but reduce the quantity imported, and thus help maintain the balance of trade in favour of this country. It is an astonishing fact that practically all the leathers analysed contain as much uncombined tannin as good quality oak or hemlock bark, and many contain much more. A table which is appended shows that approximately one-third of the tannin in these leathers is uncombined, the quantity varying from 9 to 17 per cent. This is sufficient to tan one-third as much sole leather as is now made. Fully half of this wasted tannin can and should be saved. It is worth approximately 1,000,000 dols., and would tan approximately 100,000,000 pounds of leather. This tanning material is now practically a total loss.

For the past fifteen or twenty years energetic efforts have been made to prepare from the waste liquors produced by making paper from wood by the sulphite process products that will tan hides. The woods from

which paper-pulp is made, with but few exceptions, do not contain more than from 2 to 4 per cent of tannin. If this is all removed by the sulphite liquors which are subsequently concentrated to 50 per cent solids, the concentrated material offered for tanning purposes can contain at most but 4 or 5 per cent of tannin. Up to the present efforts to make leather with waste sulphite liquors have been crowned, at most, with but indifferent success, and in no case do the makers of these products from sulphite liquors advocate that they be used alone in tanning, but always in mixture with materials of known tanning value. These materials are now receiving careful attention from several sources for determining finally whether they have a proper place in the making of leather. Until such time as it shall have been shown that these products will make serviceable leather or that they contribute to the desirable qualities of leather they should not be used in commercial tanning.

Detection of Weighting.—Although it is not practicable for the ordinary individual to determine whether the leather in shoes has been weighted or loaded, the shoe manufacturer can do so in a very simple way. Large quantities of Epsom salts give leather the characteristic bitter taste of the salts, while glucose in quantity gives the leather a very faint sweetish taste.

Whether or not leather has been loaded with soluble materials can be readily determined by anyone by the following simple procedure:—Grind a sample of the leather (a pair of soles serves well) to a coarse powder in any convenient way. The leather may be rasped, cut with a chisel or shears, ground in a mill, or sawed. Weigh 100 grms. of the ground leather on a scale that will weigh accurately to 1 gm. Place it in a small dry close-textured cotton bag which has been washed to remove the starch and other dressing materials from the fabric and which has been given an identifying mark which will not wash out in hot water. Tie securely the mouth of the bag, weigh the bag and leather carefully, and record the weight. Place it in running water as hot as can be readily borne by the hand, and wash out the soluble materials by thorough kneading for fifteen minutes. Squeeze out the water, and dry over the radiator or in any convenient way until the leather is perfectly dry. Cool and weigh again. The loss in weight represents the amount of soluble matter which has been washed out. This loss in grms. as thus determined directly represents also the percentage loss, and if this exceeds 15 per cent the leather may safely be said to be weighted.

The following figures show some results actually obtained by this method and also the results obtained in careful analysis of the leather:—

Water-soluble Material in Leather.

Sample No.	Regular analysis.	Washed out in 10 minutes.	Washed out in 20 minutes.
	Per cent.	Per cent.	Per cent.
2119	25	20	20
2127	28	24	24
2130	32	34	34
2134	25	24	24

For practical purposes the results obtained in this way are sufficiently accurate.

Bleaching of Sole Leather.

Leather which has been properly tanned with liquors made from chestnut or rock oak bark has been considered for generations to be the best for shoe soles. This leather has a bright light-oak colour, the price which it brings depending very largely on this brightness and uniformity of colour. As it comes from the tanning liquors leather is often quite irregular in colouring, and when made from nearly all other vegetable tanning materials it is darker in colour than that tanned with oak bark. Irregularity of colour is not necessarily a sign of inferiority, but, as a matter of fact, it generally indicates damage done in the preparation, tanning, or finishing

of the leather, or stained or damaged places on the original hides. The shoe manufacturer knowing that uniform colour is characteristic of hides properly prepared, tanned, and finished, and that oak bark makes a bright coloured leather, demands light uniformly coloured sole leather. The wearer of shoes also prefers leather with a good clear even colour.

To secure the higher price which this much-desired uniformity, brightness of colour, and the appearance of oak-tanned leather brings, the leather is bleached. Solutions of soda and sulphuric acid applied successively, oxalic acid, or oxalic acid and tin chloride, are the chemicals with which this is usually done. The treatment removes some of the excess tanning material from the surface and gives the leather a much lighter colour. Bleaching is especially detrimental, as the sulphuric acid is rarely completely neutralised, and consequently greatly hastens the rotting of the leather. The cost of the leather is increased by this procedure, the serviceability of the leather is decreased, and the superior appearance secured in this way permits the fraudulent sale of the leather at a higher price. The bleaching of heavy leather is the most useless and harmful of all leather-making practices, and the most vigorous efforts should be made to eliminate it.

Misbranding of Leather.

Formerly all sole leather made in this country was tanned with oak or hemlock bark, or a mixture of the two, and the leather so tanned was known as oak, hemlock, and union (oak and hemlock) respectively. More leather is tanned now with quebracho than with oak, and more with quebracho, mangrove, myrobalan, gambier, and chestnut collectively than with hemlock. Nearly half of the vegetable-tanned leather made in this country is tanned with materials other than oak and hemlock bark. Nevertheless, practically all vegetable-tanned leathers are still termed oak, hemlock, or union.

Many of the leathers are misbranded as to tannage. The tannin-free water extract from a leather tanned with chestnut oak is fluorescent when made faintly alkaline. It will be seen that the water solubles from some of the so-called oak leathers are not fluorescent; these leathers were not tanned with chestnut oak. The figures for water-soluble materials also show that many of these leathers were tanned with tanning materials other than oak or hemlock bark. Tanning liquors made from nearly all materials now used in this country, such as oak, hemlock, and mangrove barks, chestnut and gambier extracts, and myrobalan, contain approximately 2 parts of tannin to 1 part of non-tannin, not including in the non-tannin the sugars which the materials contain, which are fermented to acids, and do not, therefore, add directly to the weight of the leather. Quebracho extract, on the other hand, contains approximately 7 parts of tannin to 1 part of non-tannin.

In the last stages of tanning the leather is in contact with practically fresh normal liquors in which the relations just stated hold; therefore the tannins and non-tannins of the water-soluble extracts from leather will tend to approximate the same ratio to each other as the liquors in which it was tanned. If the sum of glucose and magnesium sulphate is subtracted from the figures for the non-tannins in any particular leather, the difference approximates the non-tannin figures for the liquor in which the final tanning of the leather was conducted. A comparison of this figure with the figures for soluble tannin shows the ratio of tannin to non-tannin in the liquor, and in many instances proves conclusively that tanning materials other than oak or hemlock bark were used; in fact the ratio indicates that quebracho was used, but no intimation of the fact is given in the branding of the leather. The branding of all leathers—"oak," "hemlock," or "union"—is deceptive, and the practice should be discontinued. No leather should be branded oak, hemlock, or union which is not tanned entirely with oak or hemlock, or a mixture of the two.

The misbranding of leather is indicated by the recent census statistics. The percentage of oak leather reported in 1909 is 7 per cent greater than in 1904, the percentage of union leather is 32 per cent greater in 1909 than in 1904, while the quantity of hemlock and oak barks and extracts used in 1909 is materially less than in 1904.

Prevention of Weighting and Bleaching.

It is improbable that the present practices of weighting and bleaching sole leather will be voluntarily discontinued by the tanner. Intelligent buying on the part of the public will do much to break up these practices. The individual purchaser of course cannot know whether the leather in the shoes he buys is weighted or has been bleached, but if he will insist that they shall not be made of weighted or bleached leather, and will not buy from those manufacturers who make such leather, the quantity of leather so treated will materially decrease, and it will be found that shoes are more durable and consequently less expensive.

The weighting and bleaching of leather may be easily and absolutely controlled by concerted action on the part of the shoe manufacturers. It is very simple for them to determine whether the sole leather delivered is weighted, and if they will refuse to buy such leather it will not be made. Shoe manufacturers will see to it that sole leather is not weighted if the public will take sufficient interest in the matter to demand unweighted leather.

NOTICES OF BOOKS.

Glycerine. By S. W. KOPPE. Translated from the German Second Edition by WILLIAM H. SIMMONS, B.Sc (Lond.). F.C.S. London: Scott, Greenwood, and Son. 1915.

THIS book has been translated from the second German edition of 1913, which was thoroughly revised and brought up to date. The production and purification of glycerin are first treated, and a full account is given of the preparation of its most important derivatives—nitroglycerin, dynamite, and lead glyceride. Its uses in the manufacture of inks, as a solvent, in soap-making, and in medicine are also discussed with a fair amount of attention to detail. The chemical analysis of glycerin and tests for various impurities are described, as well as methods of determining it in wine and beer, and a short account is given of the investigation of nitroglycerin and dynamite. A little more polish might have been given to the translation without sacrificing accuracy; it has been performed with exceeding literalness and disregard of literary style.

Woburn Experimental Station. Report on Field Experiments and Pot-culture Experiments, 1914. By J. AUGUSTUS VOELCKER, M.A., B.Sc., Ph.D. London: John Murray. 1915.

THE field and pot-culture experiments conducted during the year 1914 at the Woburn Experimental Station of the Royal Agricultural Society are described in this report. The experiments included those on the continuous growing of wheat and barley, and on the influence of magnesia upon wheat and mangolds. Some tests were also made of different varieties of cereals. Among the pot-culture experiments perhaps the most interesting were those in which Prof. Bottomley's new peat preparation for the inoculation of crops was subjected to trial. This preparation is made by first forming soluble humates, after which the material is sterilised and then inoculated with azobacter and other nitrogen-fixing organisms. It was found that the benefit of the preparation is very marked in the case of mustard; a slight advantage accrues in the case of barley, and also, as far as can be judged, with peas. The vegetative growth of tomatoes was distinctly improved, but the results in fruit with Bottomley's preparation were not so high as when ammonium nitrate was used and were slightly below those of the untreated soil.

Chemical German. By FRANCIS C. PHILLIPS. Second Edition. Easton, Pa.: The Chemical Publishing Co. London: Williams and Norgate. 1915.

THERE can be no dispute about the statement of the author of this book, that a knowledge of German is an absolutely indispensable part of the equipment of the student of chemistry, and it is also a fact that those who know a certain amount of classical German often find a difficulty in reading scientific literature. This book is intended to help such students, and it appears to be well adapted for the purpose. Comprehensive rules of nomenclature are given with exercises involving the use of terms pertaining to chemistry, both inorganic and organic, and to the apparatus and processes of the laboratory. Extracts of graduated difficulty from the writings of German chemists are also included, with a vocabulary of such words as are not likely to be found in an ordinary dictionary. A very useful list of abbreviations found in German scientific literature is also given, and some notes are added on difficulties and idioms in the extracts.

County of Northumberland Education Committee. Bulletin No. 22. Guide to Experiments for 1915. By Prof. DOUGLAS A. GILCHRIST, M.Sc. Newcastle-upon-Tyne: R. Ward and Sons.

THE work done at the Cockle Park Agricultural Station is summarised in this bulletin, from which it is clear that results of considerable importance have been obtained at the Experimental Farm. Many experiments relating to the cropping of the land, with special reference to the improvement of poor grass land, and also feeding experiments have been carried out systematically since 1896; only the former series is described in this bulletin. The general result appears to be that basic slag is the best manure to improve poor pastures on the heavy soils of Northumberland. Interesting trials of varieties of oats and barley have been conducted as well as of other crops, and valuable conclusions can be drawn from the results. The manurial requirements of rotation crops and the residual values of manures have also been thoroughly investigated, and the effects of various manures have been tested over a series of years, and thus their comparative values have been accurately ascertained.

Sul Moto dei Ioni (ed Elettroni) in un Campo Elettrico e Magnetico e su Diversi Fenomeni che ne Dipendono. ("On the Motion of Ions and Electrons in an Electric and Magnetic Field and on Various Phenomena depending on it"). By Prof. Sen. AUGUSTO RIGHI. Bologna: Gamberini e Parmeggiani. 1915.

THE subject of this pamphlet, which is reprinted from the memoirs of the R. Accademia delle Scienze dell' Istituto di Bologna, is the electronic theory relating to the forces which set in motion a conductor through which an electric current is passing when a magnetic field acts on it. The author's experiments have shown that this theory is in absolute agreement with experimental facts. The paper first gives and discusses the general formula relating to the motion of electrified particles under the action of uniform electric and magnetic fields, both when the particle is quite free and when it is subjected to molecular collisions. The formula is then applied to elucidate various phenomena, and the author's strikingly original and valuable work is clearly described, with criticisms and discussions of that of some other workers.

The Journal of Chemical Technology. Vol. II., No. 3, 1915.

THIS number of the *Journal of Chemical Technology*, which is the official organ of the Institution of Chemical Technologists, contains a full report of the meeting of the London Section, at which the subject for discussion was "The Future of British Chemical Industry." The discussion was opened by the President, Colonel C. E. Cassal, V.D., and many representative speakers took part in it,

Comparisons were made with the state of chemistry in Germany, and the status of the chemist and the attitude of the manufacturer towards him were specially considered. It is no doubt needless to say that the views expressed were thoroughly sound, and will in the main win the approval of all who have their country's welfare at heart. The issue contains some papers on miscellaneous subjects, among them one on the sugar-beet industry, in which some general information is given as to the best methods of cultivation.

Bulletin of the Imperial Institute. Vol. XIII., No. 2, 1915. London: John Murray.

THIS number of the *Bulletin of the Imperial Institute* contains a lengthy and important article on German South-West Africa, which is the third of a series dealing with the economic resources of the German colonies. The chief activities in German South-West Africa have up to the present been devoted to animal and mineral production, the cultivation of crops being of comparatively little importance; the article, however, deals with all three classes of products, and the means of internal communication and the climate are shortly discussed. A table is given showing the quantity and value of the chief exports from German South-West Africa during 1911 and 1912, together with the chief countries of destination in 1912.

CORRESPONDENCE.

THE INSTITUTION OF CHEMICAL TECHNOLOGISTS.

To the Editor of the Chemical News.

SIR,—In a recent speech delivered at a meeting of the Society of Chemical Industry, Prof. H. E. Armstrong referred to the Institution of Chemical Technologists in terms which admit of no other interpretation than that, in his view, the Institution is inimically disposed to that Society and to kindred bodies. I hope, therefore, that you will permit me through the medium of your columns to point out that statements containing any such suggestions have no foundation in fact, and can only be attributed to a complete misconception of the policy of the Institution. Although Prof. Armstrong's remarks in regard to the Institution are considerably discounted by similar unhappy gibes at the Institute of Chemistry and the Institute of Industry and Science, it is desirable that any impression possibly produced that the Institution is antagonistic to the Society of Chemical Industry or to other societies should be corrected. On the contrary, the very objects for the attainment of which the Institution was founded logically preclude the adoption of any such policy. The Institution was founded for a single purpose—one not contemplated by any of the existing societies—namely, to effect the unification and consolidation of the chemical profession. The ideal of its founders is to make

the chemical profession what has been made of law and medicine. It is obvious that such an end is not to be attained by a purely destructive policy, nor by one animated by a spirit of antagonism to other institutions. On the other hand it is equally clear that the object in view will not be secured without whole hearted and unselfish support from all branches of the chemical profession. That that support will be forthcoming, if not in the immediate present, at least in the near future, there is little reason to doubt. I make this reservation as to time because Prof. Armstrong's references to the Institution and to the Institute of Chemistry alone show, quite apart from other evidence, that there is not yet among chemists the feeling of fellowship and mutual respect for one's colleagues that is so marked a characteristic of a

properly-established profession. I am not going to deny that there is opposition to the Institution, but I am strongly of opinion that it should not be shown now. At the present moment, when even bitter political factions have come together for the common good, it is indeed unfortunate that statements should be publicly made which will sow discord in a profession of whose assistance and advice the State has so great a need. The time was never so ripe for the combination in the chemical profession that the Institution seeks to bring about. It cannot be sustained that the attainment of our end can be productive of anything but benefit, not only to the profession but to the nation, whose prosperity and even industrial existence in the future will depend on the extent to which science is applied and organised to meet the country's needs. At present the chemical profession is in the most complete state of disorganisation it is possible to conceive; it is the only profession in which such a state of things has been permitted to arise. Much younger professions have long ago set their houses in order, in recognition of the fact that they have a duty to the public as well as to themselves. I need but give two instances—the chartered accountants and the patent agents. Combination is essential in a profession if the charlatan is to be excluded and the confidence and respect of the public is to be gained. The future of chemistry as a profession, properly understood, and the position ultimately taken by it among the recognised professions will be determined entirely by the degree of loyalty exhibited by its members to each other, and the consequent benefit derived from combination and mutual support. It is true that the use of chemical science to the community is slowly being recognised, but it has needed the greatest war the world has ever known to bring about this tardy recognition. With it, however, has come no appreciation of the fact that chemistry is a learned profession, demanding years of study and experience for the attainment of proficiency. We see this in the "salaries" offered to scientific chemists, even by Government Departments rates of remuneration that an artisan would contemptuously refuse. £120 to £150 per annum is considered ample recompense for a combination of knowledge, experience, and manipulative skill when trained manual labour alone commands over double such sums. Chemists desiring to serve their country in the present crisis are expected to apply through an ordinary Labour Exchange. Recently, I saw an advertisement at one of these Exchanges for a qualified chemist side by side with an advertisement for a fish-curer. There could be few more instructive examples of the respect which the chemical profession has earned for itself. There is no need to cite the condition of chemical industry in this country, or, again, to compare what it is with what it might have been. Industry after industry has been lost, but only in obedience to the law of cause and effect. We have no right to complain. The position of our chemical industry to-day, the hopeless confusion in the chemical profession at the present moment, when it is not even known where the chemists are who possess the various forms of special experience required in this emergency, do not constitute a record of which those who regard themselves as leaders of the profession may be proud. If order is to be evolved out of chaos, if the country is to have in the future the benefit of the full resources of chemical science, the first step must be taken by chemists themselves. It is impossible for a profession to have a status in the eyes of the public and to command respect when it is split into a number of different camps, when one branch affects to look down on another as inferior, when there is no sympathy between the college and the works laboratory, and when those who have succeeded in attaining to a competence are indifferent to the struggles of their colleagues beginning their career to obtain even a living wage. The first step towards a better condition of things lies in the re-organisation of the chemical profession along the same lines as those followed by other professional men who have combined

together for the common good. There is no other way. It is at such a re-organisation that the Institution of Chemical Technologists aims. At the inception of the Institution the co-operation of the other societies was invited. It remains to be seen whether they will give us their support or whether they will tacitly or otherwise admit that the unity of the chemical profession has no meaning for them. It is, however, hard to conceive that even the opponents of the Institution can contend that the objects for which it was founded are not well worthy of achievement.—I am, &c.,

NOEL C. CASSAL,

Editor, *The Journal of Chemical Technology*; the Official Organ of the Institution of Chemical Technologists.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

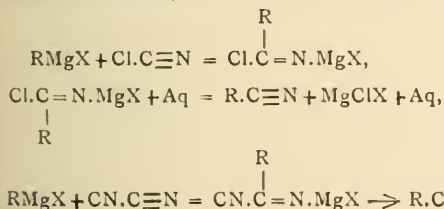
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de France.

Vol. xvii.-xviii., No. 9, 1915.

Rotatory Dispersion of Potassium Irido-oxalate.—Georges Bruhat.—Cotton has shown that absorbent active substances usually possess an abnormal rotatory dispersion in the neighbourhood of the absorption band. Drude's theory and measurements, made with different classes of coloured active substances having an asymmetrical carbon, show that the rotatory power increases very much as the absorption band is approached, reaches a maximum at the beginning of the band, then decreases very rapidly and disappears at about the centre. Its absolute value passes through a second maximum of opposite sign to the first at the other edge of the band and then decreases. This abnormal rotatory dispersion is accompanied by a phenomenon of circular dichroism; the coloured active medium absorbs the right and left circular vibrations unequally and transmits them with unequal velocities, so that a rectilinear vibration is transformed into an elliptical vibration. The ellipticity thus produced is negligible at a distance from the band and is at a maximum at the centre, the value of the maximum ellipticity being about double that of the maximum rotation. The spectropolarimetric study of active irido-oxalate of potassium confirms these conclusions, both phenomena of abnormal rotatory dispersion and circular dichroism being clearly exhibited.

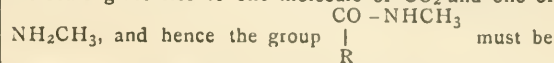
Preparation of Acetylenic Nitriles and 1-Halogen Derivatives of True Acetylenic Hydrocarbons.—V. Grignard and Cl. Courtot.—When gaseous cyanogen chloride and cyanogen act on organo-magnesium compounds nitriles are synthesised according to the equations:



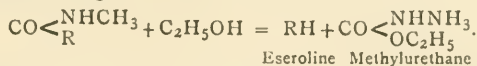
Cyanogen chloride can also act in another way, giving instead of the nitrile the chlorinated derivative of the organic radicle, $\text{RMgX} + \text{Cl} \cdot \text{N} \equiv \text{C} = \text{RCl} + (\text{C} \cdot \text{N}) \cdot \text{MgX}$. With the fatty and aromatic magnesium compounds the nitrile only is obtained, while the magnesium cyclohexanes give only the chlorinated derivative. The acetylene magnesium compounds give nitriles, the average yields being 60 to 70 per cent. If the bromide is substituted for the cyanogen chloride it functions nearly

entirely in the carbylamine form, and this gives a general method of obtaining the 1-bromo derivatives of the true acetylenic hydrocarbons.

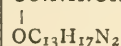
Alkaloids of Calabar Bean.—Max Polonovski.—In this paper the author, who was the first to obtain eserine, the active principle of the Calabar bean, in the solid state, gives a summary of his interrupted experiments. He has prepared the iodomethylate and sulphite of the base, and has proved that when it is decomposed by alkalis one molecule gives rise to one molecule of CO_2 and one of



present. The presence of the group CONCH_3 is proved by the fact that when eserine is heated at about 150° to 160° it liberates methyl isocyanate, which is also formed when it is oxidised. When saponified with sodium ethylate it gives eseroline and methyl urethane, the equation being—



Salway's data concerning eseroline are, on the whole, correct. Its formula is $\text{C}_{13}\text{H}_{18}\text{N}_2\text{O}$. When eserine is etherified it gives rise not to an ether of eserine but to that of eseroline. It appears that eserine is to be regarded as a methylurethane of eseroline, and its formula is $\text{CO} \cdot \text{NH} \cdot \text{CH}_3$



Geneserine, a New Alkaloid in Calabar Bean.—Max Polonovski and Charles Nitzberg.—When eserine is prepared in large quantities from Calabar bean it is often found that the melting-point of the product is too low, which indicates the presence in the plant of secondary alkaloids. To extract them the authors digested the plant with a solution of sodium bicarbonate and extracted with ether in the cold. The ether was taken up with dilute sulphuric acid, the acid solution was decomposed with sodium bicarbonate and again extracted with ether. The crystals which separated from the oil obtained fused at 128° to 129° , and consisted of a new alkaloid to which the authors gave the name geneserine. Its formula is $\text{C}_{15}\text{H}_{21}\text{N}_3\text{O}_3$. With sodium ethylate it gives a product, geneseroline, corresponding to eseroline. It is undoubtedly a new alkaloid with characteristic properties differing completely from those of eserine, into which it is very easily transformed by reduction with zinc and acetic acid.

MISCELLANEOUS.

Liebig's Extract of Meat Company, Limited.—The directors have declared a half year's dividend at the rate of 5 per cent per annum on the Preference Shares, payable less income tax at 2s. 6d. in the pound on and after October 1 to the proprietors who are registered on the 20th inst. In respect of Coupon No. 30 of the Preference Share Warrants to Bearer such dividend less income tax at 2s. 6d. in the pound will be payable on and after October 1, 1915, at the Company's Bankers, Messrs. Glyn, Mills, Currie, and Co., 67, Lombard Street, E.C.

Explosives and Foreign Shipments.—Explosives are being manufactured in enormous quantities. In Scotland the Nobel's Works at Ardeer, Ayrshire, and elsewhere, are working night and day. Ardeer is the great central factory, and is a good sized town. It extends over a thousand acres, and has its own seaport and wharfage on the Firth of Clyde. Ranges of sandhills have been utilised for the dangerous zone, which is clearly defined. Factories are grouped together in the less hazardous areas in orderly sequence—stores, workshops for all trades, timber-yards, laboratories, and offices. Railways, telephones, electric cables are throughout the works. High explosives

are shipped to all parts of the world, and stores and magazines are permanently settled abroad. Buyers are located in China, India, Japan, South Africa, Australia, and South America; in fact, wherever high explosives are wanted in large quantities. Thousands of tons are shipped yearly. One of the greatest explosions scientifically undertaken was the blowing up of the large steamer *Chatham*, which had sunk after collision in the Suez Canal, and had included in her cargo 90 tons of explosives and 16 cases of detonators. There is a large detonator factory in Stirlingshire, and in normal times about 100 million detonators are manufactured, in addition to large quantities of fulminate of mercury exported in bulk. The fuse factory is at Linlithgow, and was extended not long ago. The principal explosives manufactured are blasting gelatin, the most powerful explosive known, and specially suited for submarine mining as it is not affected by immersion in water, also gelignite, dynamite, carbonite, cambrite, and samsonite. Blasting gelatin and gelignite are extensively used in gold-mining, and have a large market in Rhodesia, New Zealand, Australia, and India. Gelignite has to a considerable extent superseded dynamite for heavy blasting. Carbonite is a permitted explosive under the Coal Mines Order, and consists of nitroglycerin absorbed in a mixture of nitrate of barium, wood-meal, nitrate of potash, and some chalk. It has established a reputation as a "safety" blasting explosive in the United Kingdom. Safety fuse is regarded as ordinary merchandise in Great Britain, and is accepted on that footing on railways and leading steamship lines. The blue sump fuse was specially made for the Australian market, but is now sold in large quantities to different parts of the world. It is thoroughly waterproof. White countered gutta-percha fuse is manufactured to meet Transvaal requirements. For export the fuse is generally packed in cases containing 300 coils each, but for South Africa 500 coils are packed in each case. Blasting gelatin contains about 93 per cent of nitroglycerin with about 7 per cent of a specially prepared nitro-cotton. Gelignite is composed of nitroglycerin, nitro-cotton, nitrate of potash, and wood-meal. Smokeless powders are for war and sporting purposes, and number cordite and ballistite. Cordite is made from nitroglycerin, gun-cotton, and mineral jelly; ballistite is made by the mixture of soluble gun-cotton with nitroglycerin and acetone. Lyddite, a powerful explosive used for filling shells fired by big guns, is melted picric acid, long known as a first-rate dye of a deep canary colour. There is practically no risk in handling these high explosives if suitable precaution is taken and the directions carefully followed, and the immense quantities shipped abroad are proof of this. Storage abroad, where State magazines are not in evidence, is readily arranged, care being taken to select a suitable site. The building should be well ventilated, free from damp, situated above the flood level of the surrounding country, with walls strong enough to resist shot from rifles. No houses or workshops should be near at hand.

Method of Detecting various Mineral and Alkaloid Poisons in Water.—Pierre Breteau.—The methods here described take less than three hours and require a litre of water. If the water is not clear it is not filtered until after it has been acidified with some drops of nitric acid, to dissolve any deposit. If there is much deposit it is best to treat the nitric acid solution of it separately. Half a litre of water is placed in a separating funnel, made alkaline with sodium carbonate solution, and shaken with 20 cc. of chloroform, which is subsequently separated off and dried with anhydrous sodium sulphate. It is then placed in two watch-glasses and evaporated on the water-bath. Then 2 cc. of 10 per cent sulphuric acid are added to each, and some drops of Bouchardat's reagent to the one and Sonnenschein's reagent to the other. The appearance of a precipitate indicates an alkaloid. If an alkaloid is present another litre of water is similarly treated, and the chloroform is divided into five portions on watch-glasses. To the first residue from evaporation five

drops of pure nitric acid are added: a red coloration indicates brucine, and violet colchicine. One drop of pure nitric acid is added to the second, which is then evaporated to dryness; this oxidation is repeated twice. An alcoholic solution of caustic potash is added to the residue: a violet coloration indicates atropine. Some drops of Fröhde's reagent are added to the third watch-glass; a violet coloration indicates morphine. Mandelin's reagent or sulphuric acid containing bichromate is added to the fourth; a violet coloration indicates strychnine. To the fifth watch-glass some drops of pure sulphuric acid are added: a persistent yellow coloration indicates colchicine, while a yellow coloration becoming carmine indicates veratrine. The alkaline water, separated from the chloroform, is acidified with acetic acid, and iron perchloride solution is added, and then ammonia drop by drop. The precipitate of iron sesquioxide containing arsenic and antimony is filtered off after boiling. If the filtered liquid is blue, copper is present. The precipitate of iron sesquioxide is washed, dissolved in sulphuric acid, and the solution is put in a hydrogen apparatus with platinised zinc and sulphuric acid. The current of gas evolved is led into silver nitrate solution. If there is a black precipitate it is dissolved in tartaric acid, warmed, acidified with HCl, and treated with H₂S. An orange precipitate is formed if antimony is present. The filtrate from the black precipitate is treated with HCl, added drop by drop, and the silver chloride is filtered off; then excess of Rougault's reagent and decinormal iodine are added: a black precipitate or a brown coloration indicates arsenic. To detect barium 2 cc. of sulphuric acid are added to half a litre of the water. Barium is absent if no precipitate has formed in five minutes. If a precipitate has formed it may be washed, treated with a solution of ammonium tartrate to eliminate lead sulphate, and then introduced on a platinum wire into a colourless flame: a green coloration indicates barium. The filtrate from the sulphuric acid precipitate is distilled with copper wire; to the distillate are added iron sulphate, iron perchloride, and soda solutions, and finally hydrochloric acid: a blue precipitate indicates cyanides. If the copper wire turns white mercury is present. The acid liquid is warmed and treated with H₂S: a black precipitate indicates mercury or lead. If on treatment with nitric acid a black insoluble residue is obtained mercury is present. Ammonia is added to the nitric acid solution and some drops of hydrogen peroxide. The liquid is filtered, the filter is washed with nitric acid and alcohol, excess of saturated sodium acetate is added to the filtered solution, and then some drops of potassium bichromate solution; if lead is present a yellow precipitate is formed. An excess of saturated sodium acetate solution is added to the liquid separated from the black sulphides, and it is then warmed and treated with sulphuretted hydrogen: a white precipitate indicates zinc. If the colour is doubtful the precipitate is filtered off, dissolved in HCl, a little sulphurous acid is added, the solution is boiled, soda solution containing potassium cyanide is added, and then sodium sulphate: a white precipitate indicates zinc.—*Journal de Pharmacie et de Chimie*, 1915, xii., No. 3.

UNIVERSITY OF SYDNEY, NEW SOUTH WALES, AUSTRALIA.

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123, Cannon Street, London, E.C.,
September 21, 1915.

THE CHEMICAL NEWS

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REDUCTION OF NITRIC OXIDE BY CONTACT ACTION OF METALS AND METALLIC OXIDES.

By BIRENDRA BHUSAN ADHIKARY.

SABATIER and Senderens have studied the direct hydrogenation of nitric oxide in presence of nickel and copper (*Comptes Rendus*, 1902, cxxxv., 278); Neogi and Adhikary have also shown that nitric oxide is reduced to ammonia in presence of reduced nickel (*Zeit. Anorg. Chem.*, 1910, lxx., 209). As the problem is an interesting one, in this paper has been studied the action of hydrogen on nitric oxide in presence of other metals. Sabatier and Senderens have shown that in presence of palladium sponge, previously saturated with hydrogen, nitric oxide is completely converted into water and ammonia (*Comptes Rendus*, 1892, cxiv., 1429). The same authors have also shown that in presence of nickel and copper (*loc. cit.*) water and ammonia are the main products formed. It has been found that ammonia and water are mainly formed in presence of some other metals, but the temperatures at which the reaction commences are different for different metals; but in all cases it has been found that when the reaction once starts it goes on when the temperature is lowered. The only explanation of this seems to be that the action is exothermic and that the heat evolved maintains the action at a lower temperature.

The mixture of nitric oxide and hydrogen was passed over gold, silver, magnesium, tin, lead, antimony, bismuth, and iron. It has been found that the yield of ammonia is greater when the metal is in a fine state of division and is freshly reduced. Sabatier and Senderens have found that oxidisable metals, like copper, iron, cadmium, zinc, are superficially oxidised by nitric oxide, and that the same metals obtained in a fine state of division by reduction in hydrogen are more readily oxidised by nitric oxide (*Comptes Rendus*, 1892, cxiv., 1429). It seems that here, in cases of easily oxidisable metals, they are alternately oxidised and reduced by means of nitric oxide and hydrogen respectively, and that nascent nitrogen combines with excess of hydrogen to form ammonia. But exceptions must be made in cases of gold and silver which are not oxidised by nitric oxide (Sabatier and Senderens, *loc. cit.*).

In cases of metallic oxides tried it has been found that oxides are first reduced to lower oxides or to metals, and these then act as catalytic agents.

Gold and Silver as Catalytic Agents.

Gold was prepared by reduction of auric chloride by ferrous sulphate. A small quantity of it (not more than 0.01 of a grm.) was heated in a tube in a nitre-bath, and the mixture of nitric oxide and hydrogen in the proportion of 1 to 3 was passed over it. Traces of ammonia began to form when the temperature of the bath was 280° C., and the action became quite perceptible at 290° C. As the reaction is exothermic the temperature inside the tube could not be strictly controlled. The action was very rapid when the temperature of the bath was kept between 335°–345° C. It was found that the yield of ammonia was almost quantitative when nitric oxide and hydrogen were mixed in the above proportion. When the same mixture was passed over gold-foil it was found that only traces of ammonia were formed.

Silver was prepared by the reduction of silver oxide. The mixture of nitric oxide and hydrogen in the above

proportion was passed over reduced silver heated in a tube in a nitre-bath. Traces of ammonia began to form at 390° C., and the action became quite perceptible when the temperature of the bath was raised above 400° C. Instead of silver, silverised asbestos (*i.e.*, asbestos soaked in a solution of silver nitrate and ignited) may be used. Blank experiments performed with asbestos alone showed that only traces of ammonia form when the mixture is passed over ignited asbestos. It was found that the yield of ammonia is quite large when the mixture of gases is passed over silver in the above proportion, the temperature of the nitre bath being 430° C.

Iron as a Catalyst.

The mixture of nitric oxide and hydrogen in the proportion of 1 to 3 was passed over iron, prepared by the reduction of iron oxide by means of hydrogen and heated in a nitre-bath. Traces of ammonia began to form at 300° C., and the action was very rapid at 350° C.

Magnesium, Zinc, and Mercury as Catalysts.

The mixture of nitric oxide and hydrogen in the proportion of 1 to 3 was passed over magnesium powders (Merck), heated in a tube-heater; only traces of ammonia were obtained, and the Nessler's solution became only slightly red.

The same mixture was passed over zinc dust (Merck), heated in a tube-heater; ammonia was obtained in large quantities, and the yield was almost quantitative.

When the same mixture was passed over mercury, heated to about 400° C., no ammonia was obtained. It may be noted here that Sabatier and Senderens (*loc. cit.*) have found that mercury vapour is not oxidised by nitric oxide.

Aluminium, Tin, and Lead as Catalysts.

The mixture of nitric oxide and hydrogen in the proportion of 1 to 3 was passed over aluminium powders (Merck); only traces of ammonia were obtained. When about two litres of the mixture were passed over aluminium Nessler's solution became only slightly red. Here also it may be noted that aluminium is not oxidised by nitric oxide (Sabatier and Senderens, *loc. cit.*).

The same mixture was passed over tin metal powders (Merck) heated in a tube heater; ammonia was obtained in large quantities and the yield was almost quantitative.

The same mixture was passed over lead-foil. Lead melted and ammonia was obtained only in small quantities. It was found that lead powders obtained by the reduction of lead oxide gave better yield of ammonia. In this case it was found that lead, though melted, remained in the form of a number of separate globules. It has generally been found that if the metal be in the liquid state better results are obtained when it is in the form of minute globules; in the latter case it may be noted that the metal presents a larger surface.

Antimony and Bismuth as Catalysts.

When the mixture of gases was passed over antimony powders (Merck) ammonia was obtained, but larger quantities were obtained when antimony powders were freshly prepared by the reduction of the oxides of antimony by means of hydrogen.

When the same mixture was passed over bismuth metal powdered, bismuth melted and no ammonia was obtained, but when bismuth powders were prepared by the reduction of bismuth oxide and the mixture passed over it large quantities of ammonia were obtained. In this case the metal, though in a liquid state, remained in the form of a number of separate globules.

Metallic Oxides as Catalysts.

The mixture of nitric oxide and hydrogen in the proportion of 1 to 3 was passed over oxides of metals belonging to Group II. of Mendeleeff's Table. When zinc oxide or

cadmium oxide were taken large quantities of ammonia were evolved, but in the case of other oxides—*e.g.*, BaO, MgO, &c.—no trace of ammonia was obtained. When mercuric oxide was used it volatilised, and no ammonia was evolved.

When the same mixture was passed over oxides of aluminium, boron, and silicon ammonia was not obtained, but when it passed over oxides of lead, tin, bismuth, and antimony ammonia evolved copiously. In the case of arsenious oxide it volatilised and no ammonia was obtained. When the mixture was passed over oxide of chromium ammonia was produced. When the same mixture passed over oxides of manganese (MnO or MnO₂) ammonia was produced in large quantities. In the case of MnO₂ it was found that the dioxide was converted into yellowish green monoxide during the reaction.

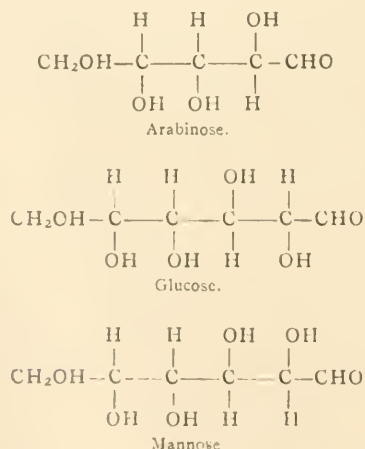
The Rajshahi College Chemical Laboratory,
Bengal, India.

CONFIGURATION IN THE SUGAR GROUP.*

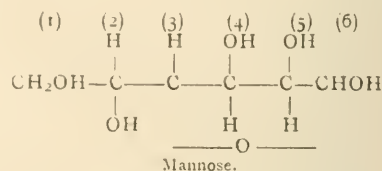
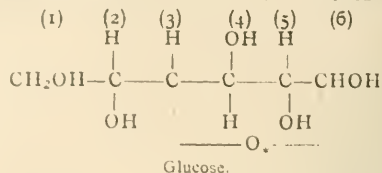
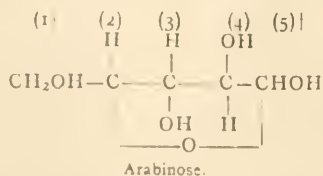
By A. HYND, M.A., D.Sc.

DURING the past twenty years the configurational formulæ for the sugars suggested by Fischer have been universally accepted and on the whole found satisfactory. From time to time, however, various irregularities and inconsistencies have been noted, and owing to meeting another of these inconsistencies the author was led to examine more closely the configuration of the simple sugars.

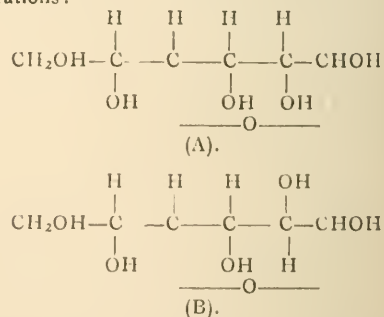
As is well known, when the cyanhydrin synthesis is applied to arabinose, the two hexoses which ultimately result are glucose and mannose. This is represented according to Fischer's system thus:—



The work of recent years, however, has shown that the sugars do not possess a free aldehydic group, but contain a closed ring system, so that the "γ-oxidic" formulæ given below are now accepted as more correct.



In the above formulæ all the three sugars are represented as having a ring consisting of four carbon atoms and one oxygen atom, and on either side of the plane formed by this ring there is a particular arrangement of hydrogen atoms and hydroxyl groups. Thus in the particular case of glucose, the above γ-oxidic structure is generally accepted as indicating that the hydroxyl group attached to carbon atom (4) and the hydrogen atoms linked to the carbon atoms (2), (3), and (5) are situated on one side of the plane of the ring—that is, the plane through the oxygen atom marked with an asterisk and the carbon atoms numbered (3), (4), (5), and (6). The author contends, however, that this is not the case, as the following consideration will show:—Starting with arabinose, the hydroxyl group attached to carbon atom (4) and the hydrogen atoms attached to carbon atoms (2) and (3) are situated on one side of the plane [2, 3, 4, 5], and during the cyanhydrin synthesis they retain that position with reference to that plane—that is, they occupy the same relative position in the resulting nitriles and hence in the corresponding acids. Now, as these acids form γ-lactones, dehydration takes place between the carboxyl group and the hydroxyl group linked to carbon atom (3), and consequently a new ring system—quite distinct from that existing in the original pentose—is thereby introduced into the structures of the latter. It is thus clear that the plane of reference must now be [3, 4, 5, 6], and as the hexoses obtained by reducing the lactones must contain the same ring system, their structures must also be referred to the plane [3, 4, 5, 6]. Working with formulæ models, it is found that, with reference to this new plane, the hexoses derived from "arabinose" have the following configurations:—



From the above it is evident that in passing from a sugar containing *n* carbon atoms to one containing (*n* + 1) carbon atoms, the plane of reference is changed, and hence it is natural to expect a change in configuration. It is to be noticed, however, that (A) and (B) are not the correct configurational formulæ for glucose and mannose, for the formula adopted for arabinose has been derived from that of erythrose without any such consideration.

Starting from the simplest sugar, namely, glyceraldehyde, the correct stereochemical formulæ for the simple

* Read before the British Association (Section B), Manchester Meeting, 1915.

+ The carbon atoms are thus indexed for reference.

sugars, polyhydric alcohols, and sugar acids containing up to ten carbon atoms have been worked out, but lack of space forbids giving these in full.

The modified system is entirely free from irregularity, and explains many experimental facts which seem impossible of explanation when Fischer's configurational formulæ are used.

THE "CRACKING" OF HYDROCARBONS.

By B. B. FREUD.

THAT carbon compounds decompose at relatively low temperatures has always been recognised as a characteristic difference between those compounds and the compounds of the other elements. That such decomposition is looked upon as an instance of the phenomenon of dissociation is not always the case. Hence it is that we have coined the special word "cracking" when discussing the formation of low boiling hydrocarbons by the action of heat energy upon higher boiling ones, while the closely analogous formation of ammonia and hydrogen chloride by heating ammonium chloride is a reaction characterised by the apparently perfectly understood word dissociation. That the mechanism of the various types of dissociation reactions is imperfectly understood is only too well known to the physical chemist. But in spite of this, when petroleum "cracking" is identified with thermal dissociation, and when the ideas of the latter are applied to the former, the chemical changes that take place in this reaction will become less mysterious. From the accidental discovery in 1861 at Newark of the "cracking" effect of high temperatures on petroleum to the recent observations of Bacon, Rittman, Snelling, Brooks, Burton, and others, all of the facts are, qualitatively at least, what we should expect from our accepted ideas of dissociation.

Hydrocarbons of smaller molecular weight are more stable than those of larger molecular weight. So it was perfectly natural to expect that since larger amounts of "kerosene" were actually obtained from a given crude oil that had been heated to a high temperature than were obtained from the same crude oil that has merely been fractionated, similarly larger amounts of "gasoline" would be obtained if the crude were subjected to a still higher temperature before fractionation. The results justified the expectation. The nature of this dissociation is not known. Nef has been explaining it for years on the basis of methylene dissociation. If we suppose our original petroleum to be composed of molecules of the formula $\text{CH}_3-(\text{CH}_2)_m-\text{CH}_2-\text{CH}_2-(\text{CH}_2)_n-\text{CH}_3$, we can imagine that dissociation might take place to form $\text{CH}_3-(\text{CH}_2)_m-\text{CH}_3$, $\text{H} \rightarrow$, and $\leftarrow \text{H}_2\text{C}(\text{CH}_2)_n-\text{CH}_3$. The $\text{H} \rightarrow$ might unite with the $\leftarrow \text{H}_2\text{C}(\text{CH}_2)_n-\text{CH}_3$ to form $\text{CH}_3(\text{CH}_2)_n\text{CH}_3$, and the alkylidene $(\text{CH}_3)(\text{CH}_2)_n-\text{CH}$ not being capable of existence, would rearrange non-reversibly to form the olefine $\text{CH}_3(\text{CH}_2)_{n-1}\text{CH}=\text{CH}_2$. Thus we have formed from a paraffin molecule two smaller ones, one a paraffin and the other an olefine. The amount of this dissociation depends upon the temperature to which the original molecule was heated. Thus we find the amount of olefine in cracked petroleum (at one atmosphere) ranging from 20 to 50 per cent, the more olefine the higher the temperature of cracking.

But the reaction need not be as simple as indicated. For instance, two of the alkyl groups $\leftarrow \text{CH}_2(\text{CH}_3)_n\text{CH}_3$ might unite to form the paraffin $\text{CH}_3(\text{CH}_2)_{2n+2}\text{CH}_3$, of a possibly greater molecular weight than the original molecule; two of the dissociated hydrogen atoms $\text{H} \rightarrow$ simultaneously would unite with one alkylidene $\text{CH}_3(\text{CH}_2)_m\text{CH} \rightarrow$ to form the paraffin $\text{H}_3(\text{CH}_2)_m\text{CH}_3$; the other alkylidene $\text{CH}_3(\text{CH}_2)_n\text{CH} \rightarrow$ would rearrange non-reversibly to the olefine $\text{CH}_3(\text{CH}_2)_{(n-1)}\text{CH}=\text{CH}_2$. Or one of the dissociated hydrogen atoms could add to

one each of the alkylidene groups to form two alkyl groups $\text{CH}_3-(\text{CH}_2)_m\text{CH}_2 \rightarrow$, which would unite to form the paraffin $\text{CH}_3(\text{CH}_2)_{2m+2}\text{CH}_3$. Thus we see that on the mere assumption of the dissociation of the paraffin molecule $\text{CH}_3(\text{CH}_2)_m\text{CH}_2\text{CH}_2(\text{CH}_2)_n\text{CH}_3$ at a definite place in the molecule we can get the paraffin molecules, $\text{CH}_3(\text{CH}_2)_n\text{CH}_3$, $\text{CH}_3(\text{CH}_2)_{2m+2}\text{CH}_3$, $\text{CH}_3(\text{CH}_2)_m\text{CH}_3$, $\text{CH}_3(\text{CH}_2)_{2m+2}\text{CH}_3$, and the olefine molecule $\text{CH}_3(\text{CH}_2)_{m-1}\text{CH}=\text{CH}_2$. When it is considered that dissociation may take place at many different places in the molecule—that is, the m and n in the illustration may be anything so long as for that molecule the m 's plus the corresponding n 's are constant, the number of possible alignments is very large. Smaller and larger molecules, paraffins, and olefines can thus be formed in the "cracking" operation, the relative amounts of the various products depending on the nature and degree of the dissociation.

Nor are the possibilities exhausted yet. It is known that olefines are in general less stable than paraffins of the same number of carbon atoms; that polymethylenes are more stable; that unsaturated hydrocarbons condense to more saturated ones, especially at higher pressures; that olefines polymerise. Hence it is to be expected that the new alignments first formed as a result of the dissociations will readjust themselves to the more stable forms under the new conditions. Thus the transformations that may take place in the "cracking" reaction are bewilderingly complex, and are followed analytically with the greatest difficulty, if at all. The evidence for this interpretation is a matter of record in the enormous literature of the subject. It is nicely summarised and extended by Brooks, Bacon, Padgett, and Humphrey, in the *Journal of Industrial and Engineering Chemistry*, vol. vii., No. 3, on the "Preparation of Gasoline and Kerosene from Heavier Hydrocarbons," from which many of the facts of this article are taken.

Having recognised that the general principle of dissociation in its broad sense applies to the "cracking" reaction, and having seen the possibility of producing large numbers and many varieties of products, it is natural to make as the next step the investigation of the influence of varying conditions on the nature of the reaction. The influence of variations in temperature and pressure, the effect of the concentration of the original molecules and the final ones, the concentration of the liquid and gas phases have all been noted; thus the subject becomes merely an application of the fundamental generalisation of heterogeneous equilibria, the phase law, and likewise of the fundamental generalisation of homogeneous equilibria, the mass action law. And since we are not necessarily keeping these variables at definite values indefinitely, or until equilibrium has been achieved in the reaction, the question of time is very important; also must be considered those factors which influence the effect of time, namely, the presence of catalysts, and the area of contact between the hot surface and the oil and between the liquid and gas phases. The developments of the "cracking" reaction culminating in the method of Rittman of having the reaction take place in the absence of the liquid phase has been due to the application of the physico chemical principles mentioned. All too often this application has been made unconsciously, but particularly in the more recent work the successes have been due to investigations based on the intentional applications of these definite considerations.

The first observation, of course, was the effect of temperature on the liquid phase at ordinary pressures. Then it was found that if the "cracking" was done at higher pressures the amount of olefine was less. Likewise at higher pressure, in spite of the higher temperature necessary to maintain it, the amount of hydrogen in the evolved gases was less. Hence the simultaneous use of higher pressures with high temperatures to get a product richer in saturated hydrocarbons than is obtained by the use of high temperature alone. Whether the smaller amounts of

olefine is a result of hydrogenation under the new conditions, as is plausible from the work of Whitaker and Rittman, or whether the saturated hydrocarbons are formed simultaneously with the appearance of the dissociated hydrogen and olefine (or alkylidene), as is indicated by Bacon, cannot be determined at present.

The first processes using increased pressure merely applied the pressure during the "cracking" operation, and subsequent distillation was effected after pressure was released. This was followed by actual distillation as well as "cracking" under pressure. Young used a pressure of 10 to 20 lbs., Krey of 2 to 4 atmospheres, Boleg of 3 to 6 atmospheres, and Bacon and Clark of 100 to 300 lbs. The success of the Burton process, at present in successful operation, is supposed to be due to this distillation under pressure. Burton claims that if the pressure valve is between the still and the condenser, thus conducting the actual distillation at ordinary pressure, large amounts of olefine are formed, while if the pressure valve is placed after the condenser, thus conducting the distillation as well as the heating at the same pressure (75 lbs.), no olefines are formed. Bacon and his collaborators question the fact that this result is due merely to the position of the valve, and their point is well taken, because we know that olefines do not polymerise under these conditions. Burton's claim is a question of fact that can easily be determined by experiment. Aside from the conflicting evidence on this point we can be sure that the efficiency of the Burton process is due to the relatively larger volumes of the vapour phase in the reaction. This conclusion is justified by Snelling's observations, mentioned later.

The next stage in the development of the "cracking" operation is the total elimination of the original liquid phase. This is one of the important conditions in the new Rittman process. In a private communication to the author Rittman says:—"The higher the pressure one uses in cracking over oil to gasoline the more saturated are the gasoline hydrocarbons produced. I have not been working at pressures exceeding 600 lbs., but up to that pressure there is a continuous advantage gained by increased pressure." In the *Scientific American* of March 20, 1915, is a description by C. H. Claudy of the Rittman method. The oil is vaporised and admitted into the reaction chamber in the form of vapour in sufficient quantity to maintain the pressure desired. In the earlier liquid vapour methods pressures of 100 lbs. are high. In the Rittman vapour method pressure of 500 lbs. is easily obtained, safe and under perfect control, as is also the temperature which is more or less uniform throughout the reaction chamber. Another important condition in the Rittman process is the removal of the products of the reaction from the reaction chamber. This of course is merely an application of the law of mass action, the removal of one of the products of the reaction so as to permit it to go to completion; thus in this process the heating and pressure are applied to the vapour phase alone, both the original and final liquid phases being eliminated from the reaction chamber. Of course the final liquid phase is subject to fractionation as usual. It will undoubtedly be found that fractionation under pressure will give the better results, for although gasoline hydrocarbons are rather stable they are slowly decomposed in the "cracking" operation and should be removed from the heavier hydrocarbons in the reduced oil under similar conditions to those under which they were formed, and also removed as soon as formed. While it should be stated that the Rittman process is only in the laboratory state, there is little doubt in the author's mind but that it will be commercially successful. This fact will soon be known definitely, as arrangements have been made whereby the Aetna Explosive Company has agreed to test and develop the process under the direction of the Bureau of Mines at a plant in Pittsburgh. The company has undertaken to devote 200,000 dols. to the investigation.

The very striking and unique claim for the Rittman process is that under similar conditions and without material change in the apparatus it is possible to obtain rather large amounts of aromatic hydrocarbons of the type of benzol and toluol, with varying quantities of mesitylene, naphthalene, and anthracene. Dr. Rittman has written the author to the effect that his "work of the last two years seems to indicate that the end-products of petroleum cracking are primarily a function of temperature, pressure, concentration, and time prevailing; in other words, one reaches the same goal regardless of the type of oil used. In other words, say at a temperature of 650° C. and 15 atmospheres pressure one obtains good yields of aromatic hydrocarbons regardless of whether he starts with an Oklahoma, a California, a Russian, or a Pennsylvania oil."

Since in the Burton process none, or but very small amounts, of aromatic hydrocarbons are produced, while in the Rittman process oil containing no aromatic hydrocarbons and passed once through the process is shown to contain as much as 6 per cent of benzol and toluol, it seems that the conditions necessary for the formation of aromatic hydrocarbons are merely higher temperature and pressure than are necessary for the formation of the gasoline hydrocarbons. This is verified by a report of the Rittman method given in the *Oil, Paint, and Drug Reporter* for March, 1915, which states that "the temperature is given for thus producing gasoline at 450° C. and above, and the pressure of about 90 lbs. per square inch, whereas with the same apparatus or process in producing larger percentages of benzol and toluol the pressure and temperatures used are increased up to the following figures—temperature 500° C. and pressures above 100 lbs. per square inch." Thus it becomes clear why the older "liquid-vapour" processes, with their limited temperature and pressure ranges, do not yield aromatic bodies, while the newer "vapour" process, with its possibility of higher temperatures and pressures, does not result in their production. The fact of the formation of aromatic bodies is not peculiar when we consider that there is no really fundamental difference between aromatic and paraffin hydrocarbons. Organic chemists have been emphasising this for many years by showing that it is possible to pass from one to the other and back again by chemical transformations, and by showing that the reactions of one class are, with a difference in degrees, the reactions of the other; also it is known that if methane is heated in the absence of air ethylene is formed, among other things; this on similar treatment gives some acetylene; likewise benzene, naphthalene, and finally carbon are formed on continuing the treatment; so there is nothing peculiar in the formation of aromatic hydrocarbons by the "cracking" process. However, as to the method of their formation, it should be said that Brooks, Bacon, &c., believe that aromatic hydrocarbons are not produced directly or indirectly by a process of dehydrogenation; they believe that benzene, toluene, and xylene split off from large so-called petroleum hydrocarbons which already contain the phenyl radicle. In this connection they refer to Jones and Wheeler, who have shown that aromatic hydrocarbons are produced in the distillation of coal at 350°, or below the temperature at which hydrogen is split off. Brooks, Bacon, &c., have also obtained aromatic hydrocarbons by the action of AlCl_3 on reduced Oklahoma oil by a sort of reversed Friedel and Crafts reaction.

Like all chemical reactions, this one can be influenced catalytically. Patents are described using steam, steam and iron, steam and other metals, metals alone, metals and hydrogen, &c., in the cracking operation. There is no doubt but that the rate of the reaction can be modified materially by catalytic agents. Exactly what the effect is quantitatively is not known yet; undoubtedly we shall hear more about this in the future. Rittman is at present working on the effect of catalysers.

That sufficient time is not given for equilibrium to be reached in these reactions is shown by the optical activity

of some of the products obtained. Kerosene fractions of most crudes show very little optical activity, while kerosene fractions of an Oklahoma oil heated at 100 lbs. pressure show this activity according to Bacon and his collaborators, who are impressed with the fact that complete racemisation has not occurred. Since these active molecules are stopping points in the readjustment of the atoms or groups set free in the cracking process, it is indeed remarkable that we have optical activity at all. The effect of time should be given much consideration in studies of this nature, for these are equilibrium reactions, and they should complete themselves before analytical operations are applied. It is because of the possible saving of time required for equilibrium to establish itself by means of catalysts that studies in this direction will be valuable.

Many of the ideas that have crystallised out of the mass of material on the subject of "cracking" appear to have been recognised by W. O. Snelling. In the *Scientific American Supplement* No. 2046 he describes some experiments which seem to emphasise the effect of the relative volume of the vapour phase. What effect his evidence will have on the questions of priority that undoubtedly will arise in patent considerations will be most interesting. Snelling has undoubtedly recognised the application of phase rule considerations, although he does not state the case as a formal one. In conclusion, the writer believes that much valuable information can be obtained if a definite heavy hydrocarbon is "cracked" under the different conditions rather than the very complex crudes. It will not be easy to get a pure body of this nature, and the analytical difficulties will be enormous, but problems as complex as this have been handled successfully, and with the commercial applications apparent it is to be expected that the work will be undertaken.—*Chemical Engineer*, xxi., No. 4.

THE FIXATION OF ATMOSPHERIC NITROGEN.*

By W. S. LANDIS.

THE author assumes that you are all more or less familiar with the use of nitrogen in one or more of its various combinations, for to catalogue even a partial list of the most common commercial nitrogen compounds would read like pages out of Olsen's "Chemical Manual" or from the *Chemiker Kalender*. He is not going to bore you with statistics of consumption of the nitrogen compounds, because the very complex nature of these statistics would make them difficult of comprehension if merely read from prepared tables, and our time can be better occupied along more interesting lines intimately connected to the subject. It is only necessary to add that in tonnage alone the nitrogen compounds stand well at the head of the list in the world's trade in heavy chemicals; nitrate of soda and sulphate of ammonia being produced in 1913 to the value of 200,000,000 dols.

Not including atmospheric nitrogen whose utilisation is yet in its infancy, we are practically dependent for our supply of this valuable element upon the nitrate deposits of Chile and its recovery as a by-product from coal. The Chilean deposits have been so frequently and fully described elsewhere that we can omit further reference to them. However, the supply of Chilean nitrate is limited and the material can be utilised for only a few purposes, such as in the manufacture of fertilisers and acids.

Ammonia, as a by-product from fuel burned in coke ovens and gas producers, is one of the most valuable forms of combination. This method of recovery will give an ever increasing supply for many centuries to come. This source of supply, however, is somewhat unsatisfactory, because a ton of coal yields only 5 to

6lbs. of ammonia as a by-product, and by-products have many limitations as a source of primary supply. This is well illustrated by the present status in Germany. There is in that country at present a considerable shortage of nitrogenous fertiliser because the Government has confiscated all stores of nitrate for military purposes. (The fertiliser industry there consumes about 800,000 tons of nitrate per year). The coke ovens, which we should expect would normally come to the rescue in such a crisis, are, however, largely closed down because industrial Germany is at a standstill, and no one wants coke. Ammonium sulphate production is, therefore, correspondingly decreased just at a time when agriculture needs it most, and its lack is felt acutely. Lately the use of coal is almost prohibited in Germany in order to force the use of coke and thus increase supply of ammonia and tar.

We come very near having the same conditions arising in this country, for were the farmer in position to take his normal fertiliser requirements there would be a great sulphate shortage, as our own industrial depression has closed down many of our coke ovens, and we would have no ready means of meeting even a normal demand for sulphate. We thus see the disadvantage of a by-product source of such an important element as nitrogen, and why inventors have turned so actively to finding a substitute for the Chilean nitrate and the coke-oven ammonia.

Naturally the inexhaustible store of atmospheric nitrogen has presented itself most prominently in this search for a new source. Neglecting the many proposals which have merely wasted much paper and ink in describing impossible methods for the fixation of atmospheric nitrogen, let us devote our attention solely to the successful, and at the present time commercially developed efforts in this field. We can classify these successful attempts into three groups:

1. Direct synthesis of nitrogen and hydrogen to ammonia.
2. Combustion of nitrogen and oxygen in the electric arc.
3. Combustion of nitrogen with metals or carbides.

The only commercial process to-day belonging to Group 1 is the so-called Haber Process. Dr. Berntsen described this process at the Eighth International Congress of Applied Chemistry, and exhibited a small working model of the apparatus. I am sorry that I can add but little to the technical information he there presented, but the owners of this process have maintained the greatest secrecy with respect to its commercial development, and but little is known in the commercial world regarding the details.

This process consists in passing a mixture of three volumes of hydrogen and one volume of nitrogen at a pressure of upwards of 150 atmospheres, over a suitable catalyst operating at a temperature of some 500° to 700° C. A single passage of this mixture through the apparatus causes a transformation of 2 to 6 per cent of the nitrogen to ammonia, which is recovered from the apparatus by condensation, and the rest of the uncombined gases are again returned to the cycle.

Too much honour cannot be shown the courageous chemists who have succeeded in placing this process on a commercial working basis. The difficulties seem almost insurmountable. The catalyst, which has taken various forms and compounds, principally metals and carbides, poisons very readily, and, therefore, extreme care must be taken in the purification of the gases. Purity which the average chemists would classify as C. P. finds no place in this industry, as that would lack almost as much of meeting the requirements of the process as the use of crude chemicals in the analytical laboratory. It took years of work to find a suitable metallic container for the high-pressure gas mixture, because of the permeability of most ordinary materials. However, most of the difficulties have all been overcome, and I have been reliably informed that the Badische Plant at Oppau supplied its

* From *The American Fertiliser*. An Address delivered before the Chemical Society of Washington, and to the Philadelphia Section of American Chemical Society, March, 1915

allotted quota of sulphate to the German Sulphate Sales Company last year, but I greatly doubt that they did it at a profit if it was made from synthetically produced ammonia, with sulphate prices as low as they were in the early part of 1914.

This process as ordinarily understood is not supposed to involve the use of any considerable quantity of electric power, which is not quite true, but does require a large amount of highly skilled labour, for the units are small and complicated. This particularly suits it to the Rhine location, but renders its value in the United States rather questionable. At Onpan, the Badische Anilin Soda Fabrik must dispose of large quantities of waste sulphuric acid, and have by-product hydrogen, hence local conditions favour the process above all others. I personally cannot see a future for its operating under American conditions, particularly in view of the competition of the much cheaper cyanamide process which furnishes the same end-product—ammonia.

The second group of processes embrace those oxidising the nitrogen of the atmosphere in the electric arc. It is well known that when air is heated to temperatures of above 1800° C. and rapidly cooled, the nitrogen oxidises to NO and remains in that form. At this temperature, however, the reaction velocity is very low and commercial working requires that temperatures of above 3000° C. be used, at which temperature the reaction velocity becomes quite considerable.

Three types of apparatus are in commercial use for performing this reaction:

1. The drum furnace with disc arc, or Birkeland Eyde.
2. The long tube furnace with spiral arc, of Schönherr.
3. The narrow furnace with fan-shaped arc, of Pauling.

There are numerous other proposed types of apparatus which are claimed to be far superior to the above, as reference to patent literature in particular will show, but the above listed three furnaces are the only ones in actual every-day operation.

The products obtained by passing air through the arc of any of these furnaces consists of a highly heated gas containing from 1 to 3 volume per cent of nitric oxide. On cooling down to temperature of approximately 600° C. this nitric oxide unites with free oxygen to form nitrogen peroxide NO₂; on further cooling of this nitrogen peroxide to below 140° C. it polymerises to N₂O₄. When brought into contact with water and oxygen, this reacts, forming a mixture of equal molecular parts of nitric and nitrous acids. By subjecting the nitrous acid to further action of the peroxide this is also changed to nitric acid with the liberation of nitric oxide, which again passes through the cycle. Thus by suitable cooling of the nitric oxide in the presence of air and water, one ultimately attains a product which consists almost quantitatively of nitric acid, and actual operating results of the large furnace plants have shown a steady recovery of about 90 per cent of the nitrogen oxides in the form of nitric acid or nitrate salts, the remainder being recovered as nitrate or not absorbed.

In general the handling of the nitrous gases from the arc furnace is now well standardised, and the design of a condensation plant is almost as well understood to day as that of a sulphuric acid plant. After passing the various systems of cooling apparatus, consisting of steam boilers, evaporators, &c., the gases enter aluminium condensers where the temperature is reduced to approximately 100° C. They then enter a preliminary oxidation chamber so proportioned that they remain in the same at least one and a-half minutes before leaving, where the preliminary oxidation to peroxide takes place. The gases next pass into a series of four or five stoneware or granite towers where they are washed with water by a counter current system, remaining in the tower system for from three to five minutes. Of the nitrogen oxidised, 90 per cent is here condensed as nitric acid, the most concentrated acid being obtained in the first tower, and averaging from 30 per cent to 35 per cent HNO₃. After passing these condensing towers, the gases usually enter a final tower fed with

caustic soda liquor, where a further 3 per cent to 5 per cent of the oxidised nitrogen is recovered as sodium nitrite. The remaining 5 per cent passes out into the air unabsorbed.

As above mentioned, these towers deliver a 30 per cent to 35 per cent nitric acid; this can be further concentrated to 50 per cent nitric acid, using the heat of the hot gases issuing from the arc furnace to perform the necessary evaporation. It is not possible to carry this evaporation much above 50 per cent for economical reasons, and where higher concentration of nitric acid is demanded special complicated concentration processes must be employed.

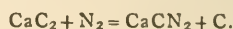
Dilute nitric acid, as obtained from the towers, finds little use in industrial processes, and it is difficult to transport. Most of the nitric acid plants, therefore, either concentrate it to 96 per cent acid by special means, or convert it into calcium nitrate for fertiliser use, or into ammonium nitrate for explosive purposes. In the latter case most of the ammonia used to-day in the nitric acid plants, operating on the arc system, is obtained from cyanamide. It is quite probable that calcium nitrate will soon disappear from the fertiliser market, as it certainly cannot be sold at a profit in competition with Chilean nitrate or ammonium sulphate, even when the latter is made from cyanamide.

As we shall see later, these arc processes require enormous quantities of cheap electric energy, and must be located near such power centres. We have no cheap power in the United States, and there is no immediate prospect of our having an arc process in continuous large scale operation within our borders. Our Western powers are far from markets and transportation of nitric acid to the East is almost out of the question.

The third group of processes embraces fixing nitrogen by metals or carbides, and has reached its highest development in the cyanamide process, which last year produced throughout the world in the fourteen factories at present operating some 300,000 tons of material, carrying over 20 per cent nitrogen.

The inventors of the cyanamide process originally attempted the synthesis of cyanides by subjecting barium carbide to the action of nitrogen, which, as is well known, forms barium cyanide. On attempting to use the cheaper calcium carbide in place of barium carbide, Doctors Frank and Caro found that instead of obtaining cyanide they obtained a new material, which proved to be calcium cyanamide. It was later found that this material could be utilised directly in agriculture, and from this discovery has grown the enormous industry which has proved to be the cheapest source of fixed atmospheric nitrogen at present in existence.

Reference to the literature existing upon the manufacture of cyanamide seems to lead one to suppose that it is a comparatively simple matter to carry out the reaction so frequently written—



This might be true to a limited extent were this the only action to contend with, but even this reaction itself is so complicated that while it is well known that it is reversible, no one has yet succeeded in correctly establishing its equilibrium constants. A laboratory study of this reaction has been carried out both in this country by Professor Thompson and abroad by Professor Haber, but neither of them has succeeded in mastering the same, because of the peculiar difficulties that arise in a study of it.

Naturally, if the highly skilled chemical laboratories met with these difficulties, we can assume that practice runs against a few of them itself. But aside from the fundamental absorption reaction, as written above, there are a number of other complications that arise in this industry, which we meet with in our every day work.

The fertiliser industry, into which most of our material at present goes, is a rather peculiar one, and probably has

more peculiar fads and precedents than almost any other highly developed industry in the country. Naturally, to sell them material, one must take into account all of the peculiarities of this industry, and must meet them, a fact which further complicates the cyanamide industry itself. You can assume that inasmuch as cyanamide is being produced and sold at the rate previously mentioned we have succeeded in meeting the requirements.

The first stage of the cyanamide process involves the production of calcium carbide. To produce, day after day, a high-grade calcium carbide that meets the peculiar requirements of the cyanamide industry, is quite an art in itself. There are no journeymen carbide workmen in our country, and we had to start out and develop our own furnaces and methods of operation. We had to seek sources of raw materials for this manufacture which are quite different from those which meet the requirements of lighting carbide, and we have to operate our furnaces in a certain peculiar way in order to combine these raw materials into a product of such structure and grade that we can make cyanamide out of it successfully. As you will recall, Moissan in his early work found that he could nitrify only certain kinds of carbide, showing that there are conditions existing in our carbide manufacture that are different from those in the manufacture of lighting carbide.

Our next great problem was to grind this special grade of calcium carbide so that it passes a hundred mesh screen. Naturally, this must be done without slaking the carbide, as hydrated lime does not make cyanamide. Now too-mesh carbide dust, when exposed to the atmosphere on a damp day, or thrown out on damp ground, is almost as explosive as low grade dynamite, so that it is quite a problem of itself to grind this carbide to the required degree of fineness.

Next comes the production of nitrogen. It is a comparatively simple matter for the chemist to make a few cubic centimetres of high grade nitrogen in his laboratory, but if one were to call upon him for two million cubic feet of a practically pure nitrogen per day, such as we make at Niagara, he would probably have to do considerable research to find out just how this enormous quantity of such high grade material could be made. In the early days of the cyanamide process, when the Niagara plant started, liquid air machinery was in a rather backward state of development, and we were forced to make our nitrogen by passing air over copper. The original plant was later enlarged. It was a long step from the combustion tube of the chemical laboratory to our present plant using retorts containing 5 tons of copper mass, but it has been successfully solved, and the new plant has been in operation with a minimum of trouble for some years. In the early days of the industry at Niagara, we could draw upon natural gas for reducing the copper oxide, so as to revivify it, but this gas supply has since failed, and we were forced to put up our own coal-gas plant. Even this coal-gas plant is not a standard one, inasmuch as we are coking coal, not only for the production of gas, but also to furnish the coke for our carbide furnaces. We are running at temperatures in our retorts and obtaining qualities of coke and gas that the average city gas plant would not consider possible of attainment.

Eventually, we had to instal purification apparatus for taking out the impurities in the nitrogen, as it came from the copper retorts, and have installed soda towers for removal of carbon dioxide, refrigeration plants for drying, lime tanks for purification, &c., and have even included a causticising plant for recovery of our spent alkali.

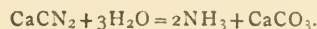
After the development of the liquid air machinery, both in the way of capacity and reliability, the problem of producing pure nitrogen was much simplified, and our latest addition at Niagara includes what was probably the largest liquid air plant in the world at the time it was built a year ago. This plant alone throws to waste almost thirty gallons of liquid air an hour, just to keep the apparatus flushed out and in good working order.

After one has overcome the difficulties in the production of a proper grade of nitrogen and of carbide, the next step is exposing these two to mutual reaction at a proper temperature, which is done in small individual ovens, holding from one-half to two and a-half tons of carbide. This reaction itself is reversible and particular precautions must be taken to keep it always running in the right direction until the carbide has all been nitrified.

The product removed from these ovens is a black, hard cake, which analyses 22 per cent nitrogen and about 1 per cent unnitrified carbide. This material, which we call lime-nitrogen, is next finely ground and stored in silos. The carbon set free in the reaction above indicated is in the form of graphite, and it is not an easy proposition to find a satisfactory mill that will grind the material fine and at the same time not blow itself up from liberated acetylene derived from the presence of any uncombined carbide, or wear itself out grinding the lime-nitrogen-graphite mixture. Extreme precautions are taken in this part of our operation, both in the mills themselves and in the elevating and conveying apparatus connected with them to avoid dangerous explosions. Thus far, not a single injury has resulted from such explosions in the cyanamide plant.

To prepare the lime nitrogen for agricultural purposes the finely ground material is partly hydrated to insure decomposition of the carbide it contains, and is then oiled to render it dustless and is stored in bulk, or packed immediately into sacks and shipped to the fertiliser mixer.

Agricultural uses, however, are not the only purposes to which the cyanamide can be applied, as it is a very simple matter to convert the cyanamide into ammonia by the exothermic reaction—



If lime nitrogen is mixed in a slurry with water and subjected to the action of heat and high pressure, it is converted quantitatively into ammonia. In this country the use of cyanamide was not developed on a large scale outside our experimental laboratory until the beginning of this year, but while I was in Germany recently, I saw in the yards of a big manufacturing concern there some 60 autoclaves, each capable of converting 10 tons of cyanamide into ammonia per day. This equipment was awaiting railroad cars to move it out, and was in no sense experimental, because three similar plants have been in operation in Germany for at least three years. The cost of this transformation is not appreciable, and the purity of the product is quite high, requiring merely passing through a rectifying column for removal of steam.

The ammonia abroad is at present being converted into a high grade sulphate and a pure nitrate, and we are at work now in this country on producing a new fertiliser material, "Ammono-Phos," consisting largely of ammonium phosphate. This product contains over 13 per cent NH_3 , and 45 to 50 per cent P_2O_5 , or over 60 per cent plant food, most of the remainder being chemically-combined water. When mixed with the high-grade potash salts, it will make a complete fertiliser three to four times as concentrated as the average grades sold to-day.

It is also possible to transform cyanamide into urea, and we have made in our experimental laboratory a considerable quantity of very pure urea.

Similarly, cyanamide can be converted into dicyandiamide by treatment with water at 90°C . This material has been proposed for use as a deterrent in explosives, but I think offers a much better field for transformation into guanidines.

These transformations of cyanamide have received a great deal of attention abroad and there are numerous derivatives on the market. Just a few months ago, I saw a sample of creatin which had been made in a chemical laboratory from cyanamide, an achievement that is not very far from the synthetic production of foods.

When a special grade of cyanamide is melted down with a flux, such as common salt, it combines the free carbon

present with the cyanamide radicle, forming cyanide. The resulting product of this fusion contains about 25 per cent of its weight in equivalent potassium cyanide; this crude form of cyanide dissolves very rapidly in water and filters rapidly from this insoluble, after which the solution is ready for metal extraction, or other uses to which cyanide in its dissolved form can be put. Large scale experiments have been tried out in a number of big cyanide plants scattered at various places throughout the world, and in every respect this material has shown an exact equivalent value to the higher grade cyanides. The transformation of the cyanamide nitrogen into cyanide nitrogen is almost quantitative, and the fusion experiments can be carried out without difficulty and at a low cost. We have here, therefore, a crude form of cyanide which can be prepared very cheaply and which could be readily delivered to the consumer at a price approximately one-third under the present prices of the higher grade cyanide. Abroad this material has been made in large quantities and transformed into pure cyanide running approximately 127 per cent potassium cyanide equivalent.

Cyanamide itself forms an excellent case hardening material, and we have prepared a number of mixtures which are in steady use at our plant for performing this operation upon various machine parts which we are using. It works rapidly and at a low temperature, but we have not yet succeeded in overcoming certain fads in large scale use of this material, and it has not met with any general introduction. We found that the case hardener is usually more concerned with the colour of his hardening powder than he is with the actual work it performs, and as the colours and odours of our cyanamide products are rather fast, we have not found it interesting to meet some of these peculiarities of the case hardening trade. While abroad, I saw these case hardening materials being prepared by the hundreds of tons for use in preparing armament and war materials, and the small factory engaged in their production has been swamped with orders ever since its inception.

The arc processes have shown themselves capable of producing nitric acid or nitrates; cyanamide itself is an entirely different product, and there has recently been evolved abroad a most successful method of oxidising this ammonia to nitric acid, so that in case of competition with the Birkeland-Eyde process, we are not entirely limited to the fixation of nitrogen, but can furnish this nitrogen in exactly the same form that their process can, and at considerably less cost. Our raw materials are cheap—coke, limestone, air. We use only one-fifth of the electrical power that the arc processes do per unit of nitrogen fixed in the form of cyanamide, in respect to ammonia, and by the addition of a very small percentage more power we can convert our cyanamide into nitric acid. We require about the same quantity of labour to fix a unit of nitrogen in cyanamide as the arc process does in nitric acid, but since there is only a small fraction more labour used to transform cyanamide nitrogen into nitric acid, we do not feel this is a great handicap when one considers our lower power consumption. On the American continent where water-powers are so expensive and so scarce this difference readily offsets the additional labour necessary to make nitric acid from cyanamide. Further, our cyanamide is easily transported, and can be changed to ammonia or nitric acid at the end of its journey at the expenditure of a small amount of steam and labour, so that we have the additional advantage in transportability of stable raw material, and subsequent conversion at the point of direct use. These commercial transformation units are small, and can easily be set up to supply even small amounts of ammonia or acid in a quite cheap and efficient plant.

There is no comparison between the initial investment required for a cyanamide plant and for an arc plant if one will include power development. The cyanamide plant per unit of nitrogen fixed requires an investment of only one-fourth that required by the arc process, and for a cyanamide-ammonia plant about one-half that required by

the Haber process. Even the combination of the cyanamide-ammonia-nitric acid process requires an investment of only one-third to one-half that for the arc process. In each case we are assuming exactly the same quantity of fixed nitrogen in the forms above designated. Where electrical power is expensive, as in the United States, there is no question regarding the superiority of the cyanamide process for the fixing of atmospheric nitrogen, particularly for fertiliser purposes, and we eventually hope that the future development of our nitric acid process will enable us to compete in every line of nitrogen compounds with all other competitive sources.—*Chemical Engineer*, xxi., No. 5.

ANALYSIS OF SPELTER.*

SPELTER ordinarily used for brass and similar alloys is usually considered in three grades: A, "High Grade;" B, "Intermediate;" and C, "Brass Special," according to the amounts of lead and other impurities present. A fourth grade, D, "Prime Western," principally used for galvanising, contains more impurities than the three grades preceding. These grades are covered by the specifications of the American Society for Testing Materials in its "Year Book" for 1913, p. 248.

The methods of sampling and analysis described below are those generally accepted in the United States for standard analysis in all the larger laboratories of both producers and consumers of zinc and zinc products. The methods of analysis are those originally proposed by Elliott and Storer (*Mem. Am. Acad. Arts and Sciences*, 1860, viii., part 1, May 20) and Price (*Chem. Engineer*, 1909, ix., 4), whose work has been checked and elaborated by the members of the Committee.

Sampling Slabs.

Select ten slabs at random from a carload and saw each slab completely across from the middle of one long side to the middle of the other, and use the sawdust as the sample, or drill three 9 mm. holes along one diagonal of each slab, boring completely through and taking care to make fine drillings. The holes should be drilled as nearly as possible at the middle and one half way between either end and the middle of such diagonals. Go over the drillings or sawings with a powerful magnet, to take out any iron which may have come from the drill or saw, and mix the sample thoroughly. The drill or saw must be thoroughly cleaned before use, and no lubricant shall be used in either drilling or sawing.

Methods of Analysis.

Lead.—The Committee considers the electrolytic and "lead acid" methods described below to be of equal merit so far as accuracy is concerned, but where laboratories are equipped for electrolysis the electrolytic method is preferred as a time saver.

Lead by Electrolytic Method.—Place 8.643 grms. of the sample in a 400 cc. beaker and add sufficient water to cover the sample; then add gradually and cautiously 30 cc. of concentrated nitric acid (sp. gr. 1.42); when the action is complete boil the solution for a few minutes to expel nitrous fumes. Wash the watch-glass and sides of the beaker and transfer the solution to a 200 cc. electrolytic beaker. Dilute to 125 cc. and electrolyse with a current of five amperes. The time required for the electrolysis is from a half to three-quarters of an hour.

* Report from a Sub-Committee on Methods of Analysis of Non-ferrous Alloys of the Division of Industrial Chemists and Chemical Engineers; Wm. B. Price (Chairman), Alden Merrill, Geo. L. Heath, Gilbert Rigg, and Bruno Wolietchowski. Approved by the Supervisory Committee on Standard Methods of Analysis, American Chemical Society.

† The empirical factor weight (8.643) is used instead of the theoretical one (8.66), as the dried dioxide is liable to contain some adherent, and included water, expelled with difficulty (*E. F. Smith's "Electro-Analysis,"* 4th edition, p. 102).

depending upon the amount of lead present in the sample. Test the solutions for complete precipitation of lead by washing the watch-glasses and sides of the beaker, so that the depth of the solution is increased about 12 mm. Then continue the current for fifteen minutes, and if the newly exposed surface is still bright the lead is completely deposited. Wash the anode three or four times with distilled water, once with alcohol, and then dry in an oven or on a hot plate at 210°C . for half an hour, and weigh.

The weight of the PbO_2 in mgrms., divided by 100, will give the percentage of lead. The PbO_2 deposit can be readily removed by covering the anode with dilute nitric acid and inserting a rod of copper.

The electrodes are cylinders of platinum gauze with 400 meshes per sq. cm. The anodes are 30 mm. in diameter by 30 mm. high, with a stem 105 mm. long of No. 16 Brown and Sharpe gauge wire (1.29 mm.), making the total height 137 mm. The cathodes are 12 mm. in diameter by 30 mm. high, with a stem 105 mm. long of No. 16 Brown and Sharpe gauge wire, making the total height 137 mm.

Lead by "Lead Acid" Method.—Place in a 350 cc. beaker 25, 15, 10, or 5 grms. of the drillings or sawings, according to whether the spelter is of Grade A, B, C, or D respectively, and add, according to the size of the sample taken, 300, 180, 120, or 60 cc. of "lead acid" (prepared as indicated in footnote below). After all but 1 gm. of the zinc is dissolved filter on a close filter and wash out the beaker a couple of times with "lead acid" from a wash-bottle. Wash the undissolved matter from the filter into the original beaker with water, and dissolve with a small amount of hot 1:1 nitric acid. Add 40 cc. of "lead acid," and evaporate until strong fumes of sulphuric acid escape. When cool add 35 cc. of water (which is the quantity of water evaporated from the "lead acid"), and heat to boiling. Add the first filtrate (containing the greater part of the zinc and possibly a small amount of lead sulphate), stir well, and allow to stand for at least five hours, preferably over night. Filter on a Gooch crucible, wash with "lead acid," then with a mixture of equal parts of alcohol and water, and finally with alcohol alone. Set the Gooch crucible inside a porcelain crucible in order to avoid reduction of lead by flame gases and mechanical disintegration of the asbestos mat. Ignite for five minutes at the full heat of a Tirrel burner. Cool and weigh as PbSO_4 .

Iron.—Place 25 grms. of zinc in a tall 700 cc. beaker and dissolve cautiously in 125 cc. of nitric acid (sp. gr. 1.42). Boil, dilute to about 300 cc., add 10 grms. of ammonium chloride, and then ammonia until the precipitated zinc hydroxide has re-dissolved. Boil, let settle, and filter on an 11-cm. S. and S. "Black Ribbon," or similar filter-paper. Wash with dilute ammonia and with hot water. Dissolve the precipitated ferric hydroxide with hot 1:4 sulphuric acid, add 40 cc. of 1:1 sulphuric acid, pass through a Jones reductor, wash first with 150 cc. of dilute sulphuric acid and then with 100 cc. of water, and titrate with potassium permanganate. (If before passing the solution through the reductor a large amount of lead sulphate is present it is well to filter it off, so as to prevent it from clogging the reductor). The potassium permanganate solution contains approximately 0.2 gm. of the crystals per litre. One cc. of permanganate solution will equal about 0.000334 gm. of iron. Run a blank with the same amounts of acid and water, and correct accordingly.

* "Lead Acid" is a solution of one volume of sulphuric acid in seven volumes of water, saturated with lead sulphate. It is prepared as follows.—300 cc. of sulphuric acid (sp. gr. 1.84) are poured into 1800 cc. of water; 1 gm. of lead acetate is dissolved in 300 cc. of water, and is added to the hot solution with stirring. The solution is allowed to settle for several days, and is syphoned off through a thick asbestos filter for use. When "lead acid" is used it is unnecessary to consider the solubility of the lead sulphate, since the solution is always brought back to the same volume as the volume of "lead acid" originally added; consequently when the lead sulphate is filtered no more lead remains in the filtrate than was originally added in the "lead acid."

Standardise the potassium permanganate against sodium oxalate. Weigh duplicate samples of sodium oxalate, 0.0200 gm. each, an amount which may require between 49 and 50 cc. of the permanganate solution. To convert sodium oxalate to iron use the factor 0.833.

Cadmium.—Place 25 grms. of drillings in a tall 500-cc. beaker, add 250 cc. of water and 55 c. of concentrated hydrochloric acid and stir. When the action has almost ceased add more acid with stirring, using about 2 cc. at a time, and allowing to stand after each addition of acid, until finally all but about 2 grms. of the zinc have been dissolved. About 60 cc. of acid in all are usually required; it is best to allow the first 55 cc. of acid to act over night. Filter, first transferring one of the undissolved pieces of zinc to the filter, and wash a couple of times with water. Discard the filtrate. Wash the undissolved matter on the filter-paper into the 500-cc. beaker, cover, and dissolve in nitric acid. Transfer to a casserole, add 20 cc. of 1:1 sulphuric acid, and evaporate until fumes appear; take up with about 100 cc. of water, boil, cool, and let settle for several hours (best over night). Filter off the lead sulphate on paper, wash with water, retain the filtrate, and discard the lead sulphate. Dilute the filtrate to 400 cc., add about 10 grms. of ammonium chloride, and pass hydrogen sulphide for one hour. It is occasionally necessary to start the precipitation of the cadmium sulphide by the addition of a drop or two of ammonia to the dilute solution. Allow to stand until the precipitate has settled, and then filter off the impure cadmium sulphide in a loose-bottomed Gooch crucible; remove the cadmium sulphide by carefully punching out the bottom into a tall 200-cc. beaker. Wipe off any cadmium sulphide remaining on the sides of the crucible, using a little asbestos pulp, add 60 cc. of 1:5 sulphuric acid and boil for one-half hour. In case of spelters carrying large amounts of cadmium it may be necessary to add more acid. The dilute acid dissolves cadmium and zinc sulphides, but not lead sulphide. Filter and dilute to 300 cc., add about 5 grms. of ammonium chloride, and precipitate with hydrogen sulphide again, in order to get rid of traces of zinc. In case a large amount of cadmium is present, a third precipitation may be necessary. After the final precipitation let settle, filter, and transfer to a weighed platinum dish, cover, and dissolve in 1:3 hydrochloric acid. Also dissolve the sulphide remaining on the filter-paper in hot 1:3 hydrochloric acid, and add it to the solution in the platinum dish. Add a little sulphuric acid, and evaporate the solution until copious fumes escape. Dilute with water, add a few cc. of concentrated nitric acid to oxidise any filter-paper shreds, and again evaporate the solution until fumes of sulphuric acid come off freely. Remove the excess of sulphuric acid by heating the dish cautiously, and finally heat to between 500° and 600°C . or to dull redness, and weigh the cadmium as sulphate.

Alternate Method for Cadmium.—Proceed as above until the cadmium sulphide has been dissolved in hydrochloric acid. Oxidise with nitric acid and filter from sulphur. Transfer the solution to a 200-cc. electrolytic beaker, add a drop or two of phenolphthalein, and then pure sodium or potassium hydroxide solution until a permanent red colour is obtained. Add a strong solution of pure potassium cyanide with constant stirring until the precipitate of cadmium hydroxide is completely dissolved. Avoid using an excess of the potassium cyanide. Dilute the solution to 150 cc., and electrolyse with a current of five amperes, using gauze electrodes of the same size as in the lead determination. The time required is one to two hours. The solution should always be tested for cadmium as follows:—Raise the liquid in the beaker, and then note after twenty minutes the newly exposed surface of the electrode. If it is still bright the cadmium is completely deposited. Next wash the electrodes with distilled water and then with alcohol. Dry at 100°C ., cool and weigh. The increase is metallic cadmium.—*Journal of Industrial and Engineering Chemistry*, vii., 547.

THE INCLUSION OF ELECTROLYTE BY
THE DEPOSIT IN THE SILVER VOLTAMETER.*

By T. W. RICHARDS and F. O. ANDEREGG.

I. Introduction.

THE silver voltameter (or better, coulometer) is an instrument of such great importance in the exact measurement of the electrical quantity that its study by many investigators is highly desirable; therefore the widespread attention which it has received during recent years is gratifying.

Since the classical researches of Lord Rayleigh and Mrs. Sidgwick (*Phil. Trans.*, A, 1884, clxxv., 411) and F. and W. Kohlrausch (*Wied. Ann.*, N. F., 1886, xxvii., 1), carried out between 1880 and 1883, the subject has been studied in many places and from many points of view. The earlier of these investigations are mentioned in detail in the description of a protracted research carried out at Harvard University, and published years ago by one of the present authors in conjunction with two assistants (Richards, Collins, and Heimrod, *Proc. Am. Acad.*, 1899, xxxv., 123; Richards and Heimrod, *Ibid.*, 1902, xxxvii., 415; also *Zeit. Phys. Chem.*, 1900, xxxii., 321; 1902, xli., 302). More recently, the National Bureau of Standards, at Washington, the National Physical Laboratory at Teddington, near London, England, and the Physikalisches Technische Reichsanstalt, at Charlottenburg, Berlin, as well as other independent physical chemists, have conducted elaborate investigations concerning the nature of several irregularities in this instrument.

The most careful of these researches have verified the main calculations brought forward in the earlier research conducted at Harvard; but unanimity has not yet been attained with regard to all the details.

Much time has been spent upon the question as to the purity of the electrolyte and the cleanliness of the apparatus, especially the porous cup recommended in the Harvard researches. These investigations were important perhaps from the standpoint of the average chemist, or especially that of the physicist unused to working with pure material, but there seems to be no important point (except perhaps the precise effect of acidification) in all this part of the recent work which was not appreciated at Harvard, fifteen years ago. No one who has worked much upon atomic weights dealing with silver nitrate solutions would think of contaminating such a solution with organic material of any kind, especially filter-paper, and there is no question that the silver nitrate used in the early Harvard work satisfied all the necessary requirements of the more recent critics. Moreover, it is obvious that a porous cup (if one is used) must be thoroughly washed free from either acid or alkali immediately before use. These patent facts might perhaps have been more emphasised instead of having been assumed almost as a matter of course, in the early Harvard paper, and if this had been done, time and trouble on the part of others might have been spared; the essential precautions were recognised long ago.

About the importance of pure materials, chemically clean apparatus, and electrically perfect insulation, there can thus be no doubt that all authorities are now agreed, the very recent work having emphasised the earlier conclusions; but concerning certain other irregularities of the silver voltameter, as has been said, there seems to be a real difference of opinion. Some of the investigators seem to think that organic impurity in the electrolyte is the only cause of excessive deposits on the cathode. That it is one of the causes there is no doubt; but it is equally clear to us that there are others. It is with regard to these points, especially, that the present work was undertaken.

The points in dispute concern, in the first place, the existence or non-existence of included mother-liquor in the

crystals deposited upon the cathode; secondly, the nature of the mother-liquor (if any) thus included; thirdly, the existence or non-existence of a surplus of silver in the liquid flowing from the anode; and, fourthly, the efficacy of a porous cup as a means of promoting exact coulometric work through the separation of the anode and the cathode.

The present paper considers the first two of these points, viz., those which concern the included mother-liquor. It was necessary to settle these before any conclusive evidence concerning the other two could be obtained; for the decision depends largely upon small differences in weight of the precipitated silver crystals, and these differences might either be caused or be masked by differences in the amount of mother-liquor included. The experiments in the three national physical laboratories seem to have under-rated the importance of this point, while exerting very praiseworthy care in other directions.

The first investigators to call attention to this very important source of error caused by inclusion of electrolyte were Lord Rayleigh and Mrs. Sidgwick. They determined the extent of the inclusion chiefly by heating the crystallised silver just short of redness. Their results showed that in many cases the inclusion of mother-liquor unquestionably takes place; moreover, there could be no question that its amount varied according to circumstances. New solutions yielded less inclusion in the crystals than the old ones, and large crystals less than small ones.

These results were entirely verified by the Harvard work carried out many years afterwards (Richards, Collins, and Heimrod, *Proc. Am. Acad.*, 1899, xxxv., 123). The magnitude of the inclusion was found to vary from 0.003 to 0.03 per cent from loss of weight on heating, and an average case was verified by analysis. The experience with silver crystals has been supported by plentiful experience with other kinds of crystals in the course of the Harvard work upon the atomic weights. Indeed, it is not too much to say that we have never been able to obtain crystals of any kind free from traces of mother-liquor, although, of course, the amount included varies greatly according to the details of crystallisation (Richards and Heimrod, *Ibid.*, 1902, xxxvii., 415; Richards, "The Inclusion and Occlusion of Solvents in Crystals," *Proc. Am. Phil. Soc.*, 1903, xlii., 28; *Zeit. Phys. Chem.*, 1903, xlvi., 189).

In spite of this experience, Gray (*Phil. Mag.*, 1886, [5], xxii., 389) and van Dijk (*Ann. d. Phys.*, 1904, xiv., 569; 1906, xix., 249) denied the existence of such included mother-liquor, and Smith, Mather, and Lowry have supported these doubters (*Phil. Trans.*, A, 1908, ccvii., 545), as well as Jaeger and von Steinwehr (*Zeit. f. Instrumentenk.*, 1908, xxviii., 327, 353). A study of these papers, however, shows that either the accuracy of the work was not adequate, or else the heating was not carried far enough to prove the point. Unquestionably, van Dijk, and Smith, Mather, and Lowry in most cases failed to use a temperature sufficiently high to drive off the inclusions, and probably this was the case also with Jaeger and von Steinwehr. Attention has already been called to the need of heating the silver to so high a point that the metal has become somewhat softened (Richards, *Proc. Am. Acad.*, 1908, xlii., 91). The mother-liquor is then set free by a series of small explosions or decrepitations, and the temperature needed is over 550°. It is quite possible, indeed, that the last traces of included matter are not expelled until the silver is completely fused (Richards, *Proc. Am. Phil. Soc.*, 1903, xlii., 28; *Zeit. Phys. Chem.*, 1903, xlvi., 189; Hulett has confirmed this inference), but very nearly all of it is driven out at dull redness, as we have repeatedly shown. In discussing their experiments on this point Jaeger and von Steinwehr make a somewhat incomprehensible correction for loss of weight of the crucible during heating. A clean platinum crucible, in our experience, heated to a temperature below redness, does not usually lose an important amount in weight, although they applied such a correction. If this doubtful

correction were omitted, their results tend to confirm ours.

The recent work carried out by the Bureau of Standards seems not to have heeded sufficiently the inclusion of mother-liquor, in spite of the arguments previously presented concerning it. More recently results which have been obtained by Hulett in careful collaboration with Duschak and with Laird (*Trans. Am. Electrochem. Soc.*, 1907, xii., 257; 1912, xii., 345) have entirely confirmed the conclusions of Lord Rayleigh, which had indeed been thoroughly verified at Harvard long before the Princeton work was begun. Hulett and his collaborators adopted van Dijk's somewhat questionable preliminary operation of scraping the crystals from the platinum dish. This is necessary if the crystals are to be heated in a tube, but it has one important disadvantage, namely, that this forcible treatment of the crystals might very well open cells containing mother-liquor which would otherwise remain closed, especially cells between the crystals and the platinum cathode. In his later work with Laird, Hulett used melted tin as a solvent for the silver; but one cannot help thinking, especially because of the large amount of carbon dioxide which he found, that dust had, during some stage of the operation, found its way into the tube. Neither of these methods (although each gives interesting results) seems to provide exactly the information desired, namely, the weight of the inclusions actually held by the deposit as weighed.

The attempt to determine the inclusions by attacking the silver deposit with mercury, as practised by the Bureau of Standards (*Bur. Standards*, 1914, *Bull.* x., 520), is likewise of uncertain value, because the solubility of silver in mercury is very slight, as we have found by careful experiment (see also Reinders, *Zeit. Phys. Chem.*, 1906, liv., 609; a saturated liquid amalgam at 20° contains only 0.04 per cent of silver), and the metal is merely converted into a solid amalgam which might withhold some of the included impurities.

For these reasons it is not necessary to discuss more fully here the interesting details of all this recent work. The very careful researches of Hulett and his collaborators substantiate that previously carried out at Harvard in showing, first, that the inclusions are often important in amount, and, secondly, that they vary considerably according to the details of experimentation. Thus, for an accurate determination of the weight of metallic silver deposited by the current the amount of inclusion must be determined in each experiment.

Nevertheless, it seemed desirable to institute new experiments touching the more essential points involved. In the course of these experiments, the weight of silver chloride obtained from the coulometric deposits was compared with the weight of silver chloride obtained from perfectly pure silver. This gives theoretically the most conclusive method of determining the amount of the impurity, but is, of course, difficult of execution. Again, crystals were ignited at high temperatures, and care was taken to find the point at which constancy of weight was attained, and also the point at which appreciable volatilisation of the silver began to invalidate the result. Yet, further, a number of deposits were scraped from their cathodes à la van Dijk and Hulett. Both crystals and cathode were washed with pure water before ignition, and it was thus found that cells containing silver nitrate solution had really been opened up by the scraping. The analyses of these crystals pointed to the same conclusion. Finally, methods for determining the amounts of inclusion having been settled, comparisons were made of the extent of inclusion involved in the various forms of the coulometer. These experiments are set forth in detail below. One does not see how any candid or unprejudiced reader, however he may have felt with regard to previous contributions on this subject, can escape the inference that inclusions in silver crystals are really important, and that no coulometric work is complete until the amount which pertains to the particular method employed is discovered by actual analysis.

II. Details concerning the Apparatus.

The porous cup coulometer as used consistently throughout this research as a standard instrument was precisely similar to that recommended by one of us in connection with G. W. Heimrod, twelve years ago (*Proc. Am. Acad.*, 1902, xxxvii., 415; *Zeit. Phys. Chem.*, 1902, xli., 302).

A large platinum crucible with a lip, weighing about 60 grms. and containing about 120 cc. was used to contain the catholyte. In it was suspended from a glass arm a small porous cylindrical Pukal cup which contained the anolyte, always kept at least 1 cm. in level below the catholyte. Everything was thoroughly insulated by glass and paraffin, and the whole was arranged under a bell-jar to protect from dust or outside impurity. The inner level was maintained constant either by a constant level syphon or by a pipette. The anodes consisted of metal carefully prepared in a pure state according to the usual method, fused in hydrogen on lime in the electric furnace (see Richards and Wells, *Journ. Am. Chem. Soc.*, 1905, xxvii., 481). They were scraped with pure sea-sand and etched with pure dilute nitric acid. In a few cases they were plated with additional silver electrolytically. The porous cups were, of course, thoroughly digested with nitric acid, and then boiled with repeated portions of the purest water until every trace of acid had been washed from their pores. In the crucial portion of the work this was done after every experiment.

The nitric acid used throughout the work was always the middle third, carefully re-distilled, of an acid already very pure.

The silver nitrate used as electrolyte was prepared either from silver made according to the method of Stas, or in the later experiments from silver precipitated by acidified ammonium formate. The salt was always crystallised twice, the first time from a slight excess of nitric acid, and the second time from pure water, a trace of acid remaining in the mother-liquor from the previous crystals. This method provides, as the work of the Bureau of Standards has shown, a solution which is free from basic salt. In some cases also solutions which had already been used in the coulometer were filtered through asbestos and then re-crystallised three times, the first two times from 10 per cent acid, and the final time as before without adding any acid. Each batch of crystals was centrifuged as usual. All the water used in the important parts of this research was purified by re-distilling first from alkaline permanganate solution, and again from a trace of sulphuric acid.

For convenience in regulating the current, an ampère meter was included in the circuit. Unless otherwise stated a current of about 0.25 ampère was used in the work. After the electrolysis was completed, the porous cup was removed and the catholyte was syphoned into a small labelled crystallising dish leaving a few cc. of the solution in the bottom of the large crucible. The occasional loose crystals of silver which either remain at the bottom or float on the surface of the electrolyte are thus kept in the original vessel. The cathode vessel was then filled with pure water, which was immediately syphoned into a large labelled dish, and this process of washing was repeated several times at even greater intervals until evening, when the crucible filled with the purest water was allowed to stand over night. On the next morning this wash-water was tested in the nephelometer with sodium chloride against pure water, to see if all the accessible silver nitrate had been washed from the pores of the crystals. In all cases, except two, this wash-water was found to be free from silver nitrate, and in these two cases another change of water left till noon showed no trace of this salt. Finally, the deposit was rinsed with very pure water, a few millilitres of which were left in the crucible. Any minute crystals of silver that may have passed over were recovered with a small platinum spatula. Our experience agrees with Hulett's, that a particle smaller than 0.01 mgrm. may be seen and recovered. The crucibles were heated two hours at 160°, after the water had been

evaporated, in electric ovens, cooled and weighed as before with all the precautions for exact weighings.

A building with its temperature regulated by thermostats, a balance very free from vibration, and favourable conditions of every kind, were of great assistance in making accurate weighings of the cathode. The weighings were regularly duplicated to within 0.02 mgrm.

(To be continued).

NOTICES OF BOOKS.

The Market for Sulphate of Ammonia and its Future.
Westminster: The Sulphate of Ammonia Association.
1915.

THE admirable foresight and acumen of the Germans in fostering the sulphate of ammonia trade are discussed in this pamphlet, which contains details of the aims of the Sulphate of Ammonia Association. It is believed that the only way to meet the menace of German methods and organisation is by the combination of British manufacturers, and it is hoped that the Association will be able to exercise considerable influence upon the world's market. In order to do so it must be representative of the whole trade, and producers can do a patriotic service of great value by joining the selling as well as the propaganda branch. It is urged that every endeavour should be made to induce British manufacturers to improve the quality of their product. The Association is encouraging experiments on the use of the salt, and it is hoped that manufacturers will be helped to weather the crisis which appears to be approaching if they will agree to cease to compete among themselves, and will loyally abide by the decisions of the experts at the head of the Association.

Hand Firing Soft Coal under Power-plant Boilers. By HENRY KREISINGER. Washington: Government Printing Office. 1915.

METHODS of using soft coal under power plant boilers are explained in this bulletin in clear non-technical language, and the best ways of handling fuel so as to get the most heat and have the least smoke are also discussed. A glossary is given of a few technical and scientific terms the use of which cannot be avoided, and stokers, firemen, &c., and those who have the task of directing them should have no difficulty in following the descriptions. Simple practical details, such as the proper position in firing, are fully discussed, and the requirements of men who have not had any scientific training are always kept in view. A short account of the process of combustion is included, and the principal heat losses in an average power plant are enumerated and the reasons for them examined.

Memoirs of the National Academy of Sciences. Vol. XII. Third Memoir, "The Turquoise." By JOSEPH E. POGUE, Ph.D. Washington, 1915.

This monograph treats very fully of the history, mineralogy, technology, and ethnology of the turquoise, and those who are interested in the study of precious stones and their relation to mankind will find it a mine of valuable information obtained from sources which are often difficult of access. In the chapter on the history of the stone it is pointed out that it was known in very remote and, indeed, prehistoric times in Egypt, and that it is mentioned in the ancient literature of almost all countries. The physical and chemical properties of turquoise are discussed fully, and some simple reactions which will be found useful in identifying it are described. The stone occurs chiefly in Persia, Central Asia, and the south-western portion of the United States, and the chapter on its origin includes a summary of its geological relations.

It is shown that like many other minerals it has more than one mode of origin; it is dominantly formed, however, by the percolation of surface water through aluminous rocks containing apatite and disseminated copper minerals. Its composition is represented by the formula $\text{CuO} \cdot 3\text{Al}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$. It has been very extensively used by the dwellers in widely separated countries, and ornaments made of it were highly prized in very early times. The question of the chalchihuitl, a green stone used by the ancient Mexicans, is discussed. The identity of this stone is not known, but the author of the monograph believes that it is fairly well established that it was either jade or green turquoise, probably the former. A chapter is devoted to the technology of the turquoise, mining, cutting, &c., and the preparation of imitations, and the monograph is provided with an excellent bibliography.

CORRESPONDENCE.

MATTER AND MASS.

To the Editor of the Chemical News.

SIR,—Concerning Mr. Loring's interesting rejoinder in your issue for August 27 (vol. cxii., pp. 99 *et seq.*) to my criticism of his former article, not to unduly prolong the discussion I will content myself with making merely two remarks touching on matters of, I think, considerable importance. And firstly, Mr. Loring now defines "quantity of matter" as equal to or identical with "mass." But in his first paper (vol. cxi., p. 301) he defined "mass" as "a term for the quantity of matter in a body." It is obvious, however, that if A is defined as equal to or identical with B, B cannot be defined as equal to or identical with A, for by so doing no information is given concerning the meaning of either term. Nor can "mass" be defined as "the product of volume and density," because the concept of "density" involves that of "mass." And secondly, I would point out that, although my criticism of Mr. Loring's treatment of the concepts "matter" and "mass" gains considerable support from experiments and theories in the domain of electricity, it is by no means dependent thereon, nor is it based upon the work and views of the modern relativistic school (for which, indeed, I have much appreciation), but is rather a simple and independent application of logic and logical rules concerning definition to the concepts in question. My greatest indebtedness, I think, is due to Prof. Ostwald.

Thanking you in anticipation for giving these remarks the hospitality of your columns, I am, &c.,

H. STANLEY REDGROVE, B.Sc., F.C.S.

West Ham Technical Institute, September 16, 1915.

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Wanted, Chief Laboratory Assistant (experienced). Wages 30s. per week. Send particulars of experience and qualifications to Mr. YATES.

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AGENT-GENERAL FOR NEW SOUTH WALES.

123, Cannon Street, London, E.C.,
September 21, 1915.

THE CHEMICAL NEWS.

VOL. CXII., No. 2915.

ANALYSIS OF TURBADIUM BRONZE.

By HOWELL WILLIAMS.

TURBADIUM bronze has recently come into use for making solid propeller castings.

It has a tensile strength of from 35 to 42 tons per square inch, and an elongation of from 14 to 20 per cent (on a two-inch test-piece).

Sea-water does not corrode it to any appreciable extent, and in this respect it has a distinct advantage over most of the alloys used for this purpose. The corrosion of a single propeller blade has been known to diminish the speed of a ship by as much as half a knot per hour.

Turbadium bronze has approximately the following composition:—

Cu	..	..	..	48.00	per cent
Zn	..	..	..	46.45	"
Sn	..	..	..	0.50	"
Pb	..	..	..	0.10	"
Fe	..	..	..	1.00	"
Al	..	..	..	0.20	"
Mn	..	..	..	1.75	"
Ni	..	..	..	2.00	"

I have recently been called upon to undertake the analysis of a large number of samples of this alloy and alloys of similar composition, and I have naturally been led to carry out experiments with a view to obtaining a method which would be both rapid and accurate.

The following method has proved most satisfactory, and is the one which I have now adopted. By means of it I can accomplish about 25 analyses per week.

1. *Tin*.—One gram. of the sample in the form of drillings (preferably not too fine) is brushed into a 200 cc. lipped beaker, dissolved in 20 cc. of HNO_3 (1.2 sp. gr.), and evaporated on a hot plate to a volume of about 10 cc. The liquid is diluted with about 50 cc. of distilled water, and allowed to stand for a short time on a cooler part of the plate, when the hydrated oxide of tin separates out as a flocculent precipitate, which is filtered on to a small ashless pulp filter, and washed free from copper with 5 per cent nitric acid water. The pulp is ignited in a porcelain crucible, brushed on to the balance-pan, and weighed as SnO_2 .

Weight $\times 78.8$ = per cent Sn.

2. *Copper*.—The filtrate and washings from the tin precipitate, which should occupy a volume of not more than 100 cc., are collected in a 150 cc. beaker, and electrolysed with a current of $\text{N.D.}_{100} = 1$ ampère and 2.5 volts, using platinum gauze electrodes with a rotating anode. The deposition of the Cu is complete in about half-an-hour. (Should it be found afterwards that a trace of copper still remains in the liquid, it can be separated in ammoniacal solution after filtering off the iron, using clean electrodes, with a current of about 0.15 ampère. This operation is seldom necessary). The mother-liquor is now removed, and the electrodes are washed with a fine jet of water from a wash-bottle. The anode is removed to a 100 cc. beaker until required. To facilitate drying, the cathode is placed in a 50 cc. beaker, and completely covered with distilled methylated spirit. After allowing to stand for a few seconds it is removed, the excess of methylated spirit evaporated, first by shaking and afterwards by placing in a steam-oven for about five minutes. The electrode is then allowed to attain room temperature in the balance case, and is weighed.

Weight $\times 100$ = per cent Cu.

3. *Lead*.—The lead is dissolved off the anode by treatment on a hot plate with a mixture consisting of 5 cc. concentrated HNO_3 , 10 cc. water, and 4 drops of methylated spirit. After removing the anode by washing with water, 3 cc. of concentrated H_2SO_4 are added to the beaker, and the mixture evaporated to fumes. The concentrated acid liquor is diluted to 30 cc. with water, and the PbSO_4 is filtered on to a prepared porcelain Gooch crucible previously weighed, and the precipitate is washed twice with a 2 per cent H_2SO_4 solution under a suction pump. The filtrate is next transferred to the beaker in which the evaporation took place, and is reserved for further use, after which the PbSO_4 is washed with methylated spirit, ignited, and weighed.

Increase in weight $\times 68.31$ = per cent Pb.

4. *Iron*.—While the operation involving the determination of the Pb is in progress the combined mother-liquor and washings from the electrolytic separation of the Cu and Pb are evaporated to a volume of about 30 cc.; 5 grms. of NH_4Cl are added, and the mixed hydroxides of Fe, Al, and Mn are precipitated by the addition of 30 cc. of saturated bromine water, followed by the addition of 30 cc. of NH_4OH (0.880 sp. gr.). The mixture is now brought to the boiling-point, and the precipitate allowed to settle, after which it is collected on a 12 cm. ashless filter, and washed with boiling water containing a little NH_4Cl and NH_4OH . The precipitate is dissolved back into the beaker in which the precipitation took place with the aid of hot dilute HCl and H_2SO_3 , the excess of SO_2 is boiled off, and the Fe oxidised with a few drops of HNO_3 . A separation of the Fe and Al from the Mn is now made by means of the well-known ammonium acetate process, and the precipitate is collected on the same filter, washed with hot water, and ignited in a porcelain crucible in front of the muffle, and weighed. After noting the weight of the precipitate it is brushed into a 500 cc. conical flask, and dissolved in 20 cc. of concentrated HCl . The Fe, after reducing with SnCl_2 solution and precipitating the excess of Sn with HgCl_2 solution, is titrated by means of $\text{N}/10 \text{ K}_2\text{Cr}_2\text{O}_7$.

1 cc. $\text{N}/10 \text{ K}_2\text{Cr}_2\text{O}_7 = 0.0056$ gm. Fe.

5. *Aluminium*.—This is obtained by subtracting the Fe calculated to Fe_2O_3 from the weight of mixed oxides.

Per cent Fe $\times 0.01428$ = weight of Fe_2O_3 .

$\text{Al}_2\text{O}_3 \times 53.03$ = per cent Al.

6. *Manganese*.—The filtrate from the PbSO_4 , which has been reserved, is treated with a little Br and NH_4OH , boiled, and filtered on to a 12 cm. ashless filter, the filtrate being rejected. The filtrate from the ammonium acetate separation is treated in the same way, the precipitate being collected on the same filter, washed with hot water, ignited, and weighed as Mn_3O_4 .

Weight $\times 72.03$ = per cent Mn.

7. *Zinc*.—Provided that the other elements have been carefully determined the figure obtained by subtracting the total percentage of elements determined from 99.9 gives a satisfactory result. In this case the Ni is determined as in 8 without further delay.

The filtrate and washings from the first separation of Fe, Al, and Mn are collected in a 200 cc. beaker, and evaporated to a bulk of about 150 cc. The solution is made neutral to litmus with CH_3COOH and 1 cc. excess is added. The Zn is now precipitated with 4 grms. $(\text{NH}_4)_2\text{PO}_4$ dissolved in a little water, and is vigorously stirred with a "policeman," after which the precipitate is allowed to settle for half-an-hour on a water-bath. The supernatant liquid is filtered through a single filter-paper, and without washing the precipitate is dissolved in 50 cc. of water and 10 cc. of HCl , made neutral with NH_4OH , and 1 cc. of CH_3COOH added. The Zn is re-precipitated, this time using only 2 grms. of $(\text{NH}_4)_2\text{PO}_4$, and after allowing to settle is filtered on to the filter-paper pre-

viously used. It is washed thoroughly with hot water and ignited in a weighed porcelain crucible, first at a low temperature and afterwards at a bright red heat, cooled, and weighed.

Weight $\times 42.91$ = per cent Zn.

8. *Nickel*.—The combined filtrates and washings from the Zn determination, which should occupy a volume of about 400 cc., are collected in a 500 cc. beaker, made slightly alkaline with NH_4OH , and heated to about 70°C . The Ni is precipitated with 15 cc. of a 1 per cent alcoholic solution of dimethylglyoxime, and after settling is collected on a 13.5 cm. common filter and washed a few times with hot water. The filter is unfolded and the precipitate washed into a weighed glass dish with a fine jet of hot water, the water is evaporated on a water-bath, and the precipitate is finally dried in a steam-bath for fifteen minutes at a temperature of 100°C ., cooled, and weighed.

Weight $\times 20.32$ = per cent Ni.

Notes.

1. The tin dioxide is almost invariably contaminated with a little iron, but the amount carried down by this method is negligible as it never exceeds 0.2 mgrm. Fe_2O_3 . The usual procedure is to evaporate to dryness, but this, apart from being quite unnecessary, leads to greater error. Not only is iron carried down in much larger quantity but also copper and lead.

2. In carrying out this operation the voltage should not be allowed to rise above 2.5, otherwise a little iron may be carried down with the copper.

3. The lead is deposited on the anode as peroxide, simultaneously with the deposition of the copper on the cathode. In the absence of manganese it can be determined directly on a weighed electrode, by first washing with methylated spirit and then heating in a muffle until the spirit burns away and re-weighing. Factor = 0.8643.

A little manganese, if present, is invariably carried down with the lead. A complete separation would be obtained by maintaining a temperature of above 70°C . throughout the electrolysis, but no time is saved by this procedure as it retards the deposition of the copper on the cathode.

4. The mixed hydroxides are washed with NH_4Cl and NH_4OH in order to remove traces of zinc.

Care should be taken not to ignite the hydroxides of Fe and Al at too high a temperature, or difficulty will be experienced in re-dissolving.

5. An alternative method could be employed. The Al in the mixed precipitate could be determined as phosphate, and the Fe obtained by difference, but this method would be more tedious.

6. The bismuthate method could also be employed with advantage, after completely removing chlorides from the precipitate by washing with hot water.

7. The figure 99.90 has been chosen instead of 100.0 in order to allow for impurities not determined, such as Bi, As, and O. I have determined these elements in a number of samples, and I find that the total averages 0.10 per cent. They are present in the following proportions:—

Bi	0.03 per cent
As	0.05 "
O	0.02 (as Cu_2O and CuO)

On looking through my totals of 127 separate analyses I find that they vary between 99.84 per cent and 99.92 per cent, so that I consider an allowance of 0.10 per cent for impurities as a reasonable and safe margin.

A double precipitation of the Zn is necessary when the quantity of Ni exceeds 1.50 per cent, as about 0.10 per cent of this element is carried down with the Zn in the first precipitation when over 1.50 per cent is present.

8. The alcoholic dimethylglyoxime is prepared by dissolving 5 grms. of the reagent in 500 cc. of methylated spirit which has been distilled between 78° and 80°C .

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BATTERY ASSAY OF COPPER.*

THE methods that follow, as given by the Committee, are those originally proposed by Heath (*Trans. Am. Inst. Min. Eng.*, 1897, xxvii., 390), whose work has been checked and elaborated by Keller, Ferguson, and members of the Committee.

The methods are those generally accepted in the United States for standard analysis in all the larger laboratories of both producers and consumers of copper and copper products.

General Instructions.

Sampling Ingots.—Select six ingots at random from the lot. Considering three ingots as a rectangular unit, drill one hole in each ingot, one at the centre, and one at each end of a diagonal of the rectangle. Drill each hole entirely through the ingot, starting from the bottom. Start the drill on the surface sufficiently to remove the oxide before commencing to collect the drillings for the sample. Run the drill so as to prevent oxidation of the chips. Discard all drillings carrying oxide from the "set" or burned by the drill. Use no lubricant on the drill, and if the sample shows oil or grease remove this with ether. Sift all drillings on a screen with 250 meshes to the sq. cm. in order to remove material which is ground between the drill and sides of the hole. Extract with a strong magnet any iron which may have come from the drill. Keep the drillings in air-tight bottles.

Weights.—Weights should be calibrated and frequently rechecked. It is recommended to use a special 5-grm. brass weight in weighing the samples, and to have the weight of the sample always within 5 mgrms. of 5 grms. (Greenwood, U.S. Metals Refinery Co., personal communication). When the cathode with its deposit is finally weighed the identical weights are to be used with which the cylinder was tared, plus the special 5-grm. brass weight. This brings all the change or deficiency in the final weight on a small fractional weight and the beam and rider.

Electrodes.—The cathode is a platinum sheet of 5×10 cm., giving a depositing surface, counting both sides, of 100 sq. cm. This sheet is formed into a cylinder of the open type, and the stem is riveted and soldered with gold to the middle of the sheet. There should be no seam which cannot be cleansed completely by two washings. The anode is made from 1-mm. platinum wire, formed into a spiral of seven turns, having a diameter of 12.5 mm. and a height of 38 mm., the stem being straight and 125 mm. long.

Electrolytic and Low resistance Lake Copper.

The method described below is applicable to such grades of copper as are covered by the specifications of the American Society for Testing Materials, as given in its "Year Book" for 1913, p. 241. The silver is deposited with the copper and is included as such; when it is desired to correct for the silver this is determined in a larger separate sample, and the amount found is deducted from the deposit of copper plus silver. The deposition of the silver with the copper is said to work well up to the limit of 0.3 per cent silver, or 100 ounces per ton. All assays are to be made in duplicate and must check within an outside limit of 0.015 per cent.

Method of Analysis.—Place 5 grms. of the drillings in a tall lipless beaker which is provided with a well-fitting cover-glass, and add a mixture of 7 cc. of nitric acid (1.42 sp. gr.), 10 cc. of sulphuric acid (1.84 sp. gr.), and 25 cc. of water. This mixture is used as a stock "Assay

* Report from a Sub-Committee on Methods of Analysis of Non-ferrous Alloys of the Division of Industrial Chemists and Chemical Engineers; Wm. B. Price (Chairman), Alden Merrill, Geo. L. Heath, Gilbert Rigg, and Bruno Woiciechowski. Approved by the Supervisory Committee on Standard Methods of Analysis, American Chemical Society. From the *Journal of Industrial and Engineering Chemistry*, vii., No. 6.

Solution," 42 cc. being measured for each sample (Note 1). The electrolysis beakers are from 100 to 125 mm. tall and 55 mm. in diameter across the bottom, with a total capacity of 225 to 300 cc. After the assays have stood for a few minutes and the action has nearly ceased place them on a steam bath having a temperature of 80 to 90° C., and allow them to remain there until solution is completed and the red fumes have disappeared. Wash the cover and the sides of the beaker and dilute the solution to 150 cc. and electrolyse.

During electrolysis the beakers are covered with two pairs of split watch glasses placed at right angles to each other. The current in each solution should be 1 ampère, which will require about 10 volts if the assays are arranged in parallel (Note 2). It is convenient to start the assays at night; after about fifteen hours wash the cover-glasses, electrodes, and beakers, and reduce the current to 0.6 ampère per solution. As soon as the cathodes begin to evolve gas reduce the current to 0.4 ampère per solution. When this occurs take out about 1 cc. of liquid, place it in a depression in a porcelain test-plate, and add two or three drops of fresh hydrogen sulphide water. If the slightest discoloration occurs continue the electrolysis, repeating the test until there is no discoloration whatever (Note 3). If possible the assay should finish without decided evolution of gas.

Without interrupting the current syphon off the acid solution, at the same time filling the beakers with distilled water. Remove the cathodes quickly and rinse them in distilled water and two successive baths of alcohol. An experienced operator can quickly remove a cathode and immerse it in water without loss. Throw off the excess alcohol by a quick motion of the hand and ignite the remainder by bringing the cathode quickly to the flame of an alcohol lamp; then keep the cathode moving continually while the alcohol burns. This method of burning off the alcohol dries the cathode without causing oxidation, whereas drying in an oven at 100° C. generally causes increase in weight.

Low-grade or Casting Copper.

For all grades of copper which are not included in the specifications of the American Society for Testing Materials as Electrolytic and Low-resistance Lake Copper the procedures given below are recommended. These brands may contain a considerable amount of arsenic and some antimony, tellurium, bismuth, and nickel. All assays are made in duplicate and must check within an outside limit of 0.015 per cent.

It has been recommended to use with solutions of these coppers about 2 cc. of an addition agent prepared by boiling "hard oil" with strong nitric acid, cooling, and removing the grease (Guess, *Trans. Am. Inst. Min. Eng.*, 1905, xxxvi., 605). This, it is said, will permit the use of high current densities and yet allow the copper to be deposited pure and bright. Moreover, it is said that arsenic and antimony when present do not contaminate the copper. It seems probable, however (Keller, *Ibid.*, 1913, 2099, *Bul. So.*; Heath, *Journ. Ind. and Eng. Chem.*, 1911, iii., 75), that copper deposited from such solutions is not quite pure, and that it is more accurate to purify the cathode deposit (Modification I. below) or to give a preliminary treatment to the solution (Modification II.).

The Committee gives preference to Modification II., and Modification I. should be used only in the presence of small amounts of impurities.

Modification I.—Carry out the assay exactly as given for Electrolytic and Low-resistance Lake Copper. Place the cathode in a clean beaker, cover with a watch-glass perforated with a small hole just large enough to accommodate the stem of the electrode, add 42 cc. of stock "Assay Solution" and water enough to cover the sheet. Let it stand upon the steam bath until the coating is dissolved; re-electrolyse in the regular manner.

Modification II. (Heath, Senter modified, *Journ. Am.*

Chem. Soc., 1904, xxvi., 1123).—Dissolve a 5 grm. sample in 42 cc. of the "Assay Solution" and evaporate until all the nitric acid is expelled; re-dissolve in 70 cc. water and add 3 cc. ferric nitrate solution (1 cc.=0.01 grm. iron). Transfer the solution to a lipped beaker and place the original beaker under a funnel fitted with a small filter-paper. Precipitate the iron from the hot liquid by ammonia, filter, and wash out salts. Place the solution on a hot plate to concentrate, re-precipitate the hydroxide from dilute sulphuric acid in a very small volume of solution, and add the filtrate to the main solution. Re-precipitate the hydroxide once more from dilute sulphuric acid, filter, wash thoroughly, and add the filtrate to the main solution. Make acid with dilute sulphuric acid and add 2 cc. of nitric acid (1.42 sp. gr.). Deposit the copper as in the method for Electrolytic and Low-resistance Lake Copper.

Modification III. (Heath, *Ibid.*, 1914, xxvi., 1123; Keller, *Trans. Am. Inst. Min. Eng.*, 1913, 2098, *Bul. Ixxx.* For copper containing only traces of antimony or bismuth, but sufficient selenium or tellurium to interfere).—Dissolve the 5-grm. sample in 42 cc. of "Assay Solution" and evaporate until fumes appear or until the residue is white. Re-dissolve in 60 cc. of water and saturate the boiling hot solution for ten minutes with sulphur dioxide gas, removing the solution from the lamp when the gas is started. The gas may be generated by dropping cold saturated sodium sulphite solution into strong sulphuric acid. It is also conveniently obtainable in cylinders, which are fitted with a valve. Let the precipitate settle for a few hours, filter, and wash with a little hot water. Boil the filtrate gently, to remove most of the sulphur dioxide gas. Ignite the filter in a porcelain crucible to volatilise the selenium (Note 4) and tellurium; re-dissolve the oxidised residue in 1.5—2 cc. of nitric acid and add to the main solution. Deposit the copper as in the method for Electrolytic and Low-resistance Lake Copper.

Modification IV. (A—Heath, *Journ. Am. Chem. Soc.*, 1904, xxvi., 1124. B—Heath, *Journ. Ind. and Eng. Chem.*, 1911, iii., 75. For copper high in arsenic only). The Committee gives preference to B.

A.—Dissolve the sample in 42 cc. of the "Assay Solution" in the regular way, and add 5 grms. of ammonium nitrate; electrolyse as usual.

B.—Dissolve the sample in 60 cc. of the "Assay Solution" instead of 42 cc.; electrolyse as usual.

Notes.

1. Use of the dilute solution above described prevents a violent reaction and a consequent loss of copper with the vapours. The solution should not be boiled, since this likewise may cause a loss of copper.

2. By the use of rotating anodes, gauze or perforated electrodes, or the Friary solenoid, it is possible to use a high-current density and to reduce the time required for depositing the copper to about four hours. Good results can be obtained by experienced workers, but there is much more chance for error. The slow, or overnight method, which is more certain and requires less of the operator's time, is therefore recommended.

3. It has been shown by Heath (*Journ. Ind. and Eng. Chem.*, 1912, iv., 404) that a few thousandths of a percent of copper may remain in the solution without being detected by the hydrogen sulphide test on the spot plate. This amount of copper is negligible in many instances, but when necessary to make exact determinations, as in the complete analysis of copper, make the solution after electrolysis slightly alkaline, neutralise with hydrochloric acid (1.19 sp. gr.), adding 3 cc. excess, evaporate to 50 cc., and precipitate with hydrogen sulphide. Filter off the copper sulphide, treat with nitric and sulphuric acids, and deposit the small amount of copper from the solution by electrolysis, and add it to that obtained in the original determination.

4. The selenium is said to be carried down by sulphur dioxide as a selenide of silver, but the roasting sufficiently removes the elements selenium and tellurium. When silver is to be removed, the selenium, &c., are thrown down with the silver by the sulphur dioxide gas, and the precipitation of silver is then completed by the addition of chlorides or hydrochloric acid.

A COMPARISON OF THE RELATIVE DRYING POWERS OF SULPHURIC ACID, CALCIUM CHLORIDE, AND ALUMINIUM TRIOXIDE WHEN USED IN ORDINARY SCHEIBLER DESICCATING JARS.*

By J. W. MARDEN and VANNA ELLIOT.

IN spite of the many objections put forward to CaCl_2 and H_2SO_4 for ordinary desiccating purposes, these substances are still quite generally used. Nearly every analyst knows from experience that if a perfectly dry sample of coal, for example, is placed in a desiccator containing CaCl_2 which has been used for some time, or concentrated H_2SO_4 , the coal will increase in weight. When the desiccator is opened some moisture enters from the atmosphere, to be sure, but not enough to account for the increase in weight of the coal.

As compared to the wide use to which H_2SO_4 and CaCl_2 are put as drying agents for organic substances which cannot be heated, the literature on the subject is meagre. The desiccating efficiency of several substances, like CaCl_2 , Na, fused NaOH , P_2O_5 , &c., has been tried. Baxter and Warren tried CaBr_2 , ZnBr_2 , and ZnCl_2 by passing moist air over them (*Journ. Am. Chem. Soc.*, 1911, xxxiii., 340). They found that H_2SO_4 was more efficient than any of these. Johnson has published a note on the use of Al_2O_3 as a desiccating agent, in which it is claimed that Al_2O_3 is more effective than H_2SO_4 for removing moisture from air saturated with water vapour (*Ibid.*, 1912, xxxiv., 912).

In the hope of suggesting a good substitute for the time-worn CaCl_2 if not for H_2SO_4 in ordinary desiccation the present work was undertaken; also a series of experiments with H_2SO_4 has been run to show the effect of the concentration of the acid on drying certain substances, and it is hoped that the results will throw some light on the vagaries of H_2SO_4 as a desiccant. Many analysts seem in doubt regarding the total amount of moisture that is obtained by H_2SO_4 drying; some have the opinion that they get all but two or three-hundredths of 1 per cent in most cases, while others think that they obtain very much less than that percentage of moisture. At best any drying method with H_2SO_4 can be only an arbitrary one. Since this is an old subject most of the experimental work for this paper is given in abstract.

Many experiments have shown that from certain substances all of the moisture cannot be obtained by the ordinary H_2SO_4 drying method at 25°C . A sample of pure sugar syrup, for example, containing 49.89 per cent moisture, mixed with ten times its weight of sand, yields an average of about 48.17 per cent moisture. With maple syrup, even with vacuum, the same condition is observed. The percentage of moisture obtained by H_2SO_4 drying is less than that obtained by the refractive index or by heating at 100°C . This behaviour of sugar, although somewhat exaggerated, is typical of the behaviour of other substances. The water-vapour pressure of some materials still containing residual moisture is as low as that of the H_2SO_4 over which they have been dried. It has been shown that considerable amounts of H_2SO_4 distil off in vacuum, and for this reason Gore suggests the use of CaO

for high vacuums (*Journ. Biol. Chem.*, xv., 259). By graphic interpolation, concentrated (95 per cent) H_2SO_4 has a vapour pressure of about 0.03 mm. at 25°C .

According to Thorpe the speed of drying is hastened, but no more moisture is obtained by the use of vacuum ("Dictionary of Applied Chemistry," 1912, ii., 210). In a series of trials with cheese, syrup, coffee, &c., using both H_2SO_4 and CaCl_2 , slightly more moisture was obtained with vacuum than without.

In one instance it was as much as 0.7 per cent and in other cases quite small.

The effect of a fairly large variation in the concentration of H_2SO_4 changes the total amount of moisture removed from some substances very slightly; in other cases, however, the change is marked. Table I. shows the results obtained with flour, cane-sugar syrup, and cheese dried to constant weight over various concentrations of H_2SO_4 . Each sample for each concentration was dried in an individual desiccator.

TABLE I.—Effect of Concentration on Drying Power of H_2SO_4 . Atmospheric Pressure and Laboratory Temperature. Total time of drying, about three weeks.

Per cent H_2SO_4 .	Vapour pressure mm. of Hg (approximate).	Per cent water in		
		White flour.	Cane syrup.	Cheese.
95.0	0.03?	12.48	48.28	26.51
84.8	0.18	12.28	48.25	26.10
78.3	0.8	10.04	48.27	25.58
65.6	2.7	7.22	48.10	24.88
62.6	3.5	2.89	47.97	23.47
37.0	15.0	0.10	47.30	21.18
29.6	17.5	—	34.70	—
21.9	20.0	—	22.01	—
15.2	21.0	—	0.29	—
7.0	22.5	—	49.4 inc. in weight	—
Per cent moisture found by drying at 100°C . to constant weight				
		11.85	49.78	26.65
Polariscope		—	49.89	—
100 per cent (a) H_2SO_4 ..		12.55	48.28	26.65

(a) Values obtained by plotting percentage moisture against percentage H_2SO_4 .

It will be seen from Table I. that cane syrup could be dried about as well, although, as laboratory experience showed, not as quickly, over 75 per cent as over 100 per cent H_2SO_4 . With cheese the percentage of moisture obtained over 100 per cent H_2SO_4 is about the same as that by drying to constant weight at 100°C . Flour shows another example of the increase in weight of some materials on heating, due to a certain amount of oxidation. Skertchly has pointed out inconsistencies of this kind which he found while drying biscuits (*Journ. Soc. Chem. Ind.*, January, 1913).

As has been suggested by several authors, exposing a substance over varying concentrations of H_2SO_4 , and finding the concentration at which it neither gains nor loses weight, indicates the concentration of H_2SO_4 , which has the same vapour pressure as the material. In this way flour has a vapour pressure of about 15.0 mm. and cane-sugar syrup of about 21.0 mm.

Hempel has shown that the rate at which substances dry depends upon the rate which water vapour is transferred (*Ber.*, 1890, xxiii., 3566). Since air saturated with water vapour is less dense than unsaturated air, Hempel puts the H_2SO_4 in the upper part of the desiccating jar. Similarly, if air currents can be formed in the jar the drying will go much faster. To show this point, samples of maple syrup were dried over 95 per cent H_2SO_4 at room temperature in two desiccators; in one a small motor was introduced and the air stirred vigorously during the experiment. In one and one-half hours as

* This work was started in the Laboratory of the South Dakota State Food and Drug Department

much moisture was removed with stirring as was removed without stirring in six hours.

Several portions of Al_2O_3 were prepared for comparison with the other desiccants. The Al_2O_3 used in the preliminary trials was prepared from "technical" $\text{Al}_2(\text{SO}_4)_3$ by dissolving the salt in water and precipitating the $\text{Al}(\text{OH})_3$ with NH_4OH . The aluminium hydroxide was filtered off and dehydrated in the glass tube of a combustion furnace with the smoky flame. The Al_2O_3 employed in the later experiments was made in the same way, except that "C. P." $\text{Al}_2(\text{SO}_4)_3$ was used in the preparation and the $\text{Al}(\text{OH})_3$ was washed many times to remove any impurity which might lead to erroneous results.

Preliminary experiments comparing Al_2O_3 with CaCl_2 showed that in nine days at laboratory temperature and pressure a sample of coffee yielded 0.2 per cent more moisture over Al_2O_3 than over CaCl_2 . In the same length of time a sample of sugar yielded the same weight of moisture over either. The percentage of moisture in this case, however, was very low. Trials were made also by placing weighed dishes of Al_2O_3 over H_2SO_4 and H_2SO_4 over Al_2O_3 , to see which would increase in weight more rapidly. The moisture introduced by opening the desiccator was enough to vitiate the results somewhat, but the Al_2O_3 increased in weight faster than the H_2SO_4 . Table II. shows the percentage of moisture obtained with three common materials dried over the three desiccants and kept in a thermostat at 25°C . Each percentage shown is the average result of duplicate experiments in individual desiccators over the same weight of desiccant.

The time values in Table II. are given roughly in days, which intervals are close enough to show the points in question. Some of the moisture in the blue vitriol was lost in grinding the sample.

TABLE II.—Percentage of Moisture by Different Desiccants.

Days.	Flour.			$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$			Coffee.	
	Al_2O_3	H_2SO_4 95 per cent.	CaCl_2	Al_2O_3	H_2SO_4 95 per cent.	CaCl_2	Al_2O_3	CaCl_2
1	8.42	8.42	8.47	14.12	15.08	15.22	1.31	1.17
2	9.51	9.56	9.21	18.76	19.47	16.84	1.98	1.82
3	10.30	10.33	10.06	23.73	25.51	21.31	2.66	2.38
4	10.67	10.61	10.35	28.11	28.74	25.10	3.11	2.92
5	11.08	10.96	10.62	29.36	29.46	28.77	3.30	3.11
6	11.21	11.13	10.75	29.43	29.45	29.32	3.44	3.22
7	11.46	11.33	10.96	29.53	29.54	29.42	3.54	3.32
8	—	—	—	—	—	—	3.66	3.46
10	—	—	—	29.53	29.54	29.42	—	—
11	11.75	11.64	11.15	—	—	—	—	3.46
13	11.75	11.64	11.15	29.53	29.54	29.42	—	—

The work in Table II. was repeated in vacuum desiccators at a pressure of about one-tenth atmosphere and at laboratory temperatures. As before, three substances—flour, blue vitriol, and tea—were dried over the three desiccants. Although there was some difficulty in obtaining desiccating jars with the same power for "holding" the vacuum, the average results were in the same order as in Table II. For small amounts of moisture Al_2O_3 appears to be somewhat superior to either H_2SO_4 or CaCl_2 when used in this way, while with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, which has a larger percentage of moisture, there seems to be but little choice between Al_2O_3 and 95 per cent H_2SO_4 . CaCl_2 seems to be inferior to either of the others. It is possible that H_2SO_4 methods of drying may give better results when the acid has frequent agitation and when two or three charges of fresh acid are added during a determination. Al_2O_3 has the further advantages that one need not guard against slopping, burns, &c., as when using H_2SO_4 , and that this oxide can be re-heated when it becomes saturated with water and used again and again.

—*Journal of Industrial and Engineering Chemistry.*

TITANIUM AND ITS EFFECTS ON STEEL.

By GEO. F. COMSTOCK.

TITANIUM is widely distributed in the earth's crust in small quantities and is always found as an oxide, its principal ores being rutile, the fairly purely dioxide and ilmenite, a mixture of iron and titanium oxides. One of its chief peculiarities is the readiness with which it combines with nitrogen. It is one of the very few elements which will "burn" in an atmosphere of nitrogen. Its dioxide is one of the most stable compounds known, and great energy is required to decompose it. Thus it follows that when titanium is separated from its oxygen, it will readily re-combine with it, with evolution of heat. The value of titanium in the steel industry is due largely to the fact that its dioxide is so much more stable than iron oxide that its action in "deoxidising" melted steel is very powerful.

The reduction of the natural oxides is effected either by reduction with carbon by means of the electric arc or by an aluminothermic reaction. The former process delivers the titanium in the form of the carbide, while the latter produces an alloy of titanium, aluminium, and iron. The carbide is the form most generally used.

Metallic titanium when heated to redness in nitrogen forms titanium nitride, but when heated in air only the oxide is formed. The nitride is slowly converted to the oxide when heated to redness in air, but the carbide burns vigorously in air, forming dioxide. The reverse reaction takes place only at very high temperatures. Even at the temperature of the blast-furnace titaniferous ores do not give more than 1 per cent of titanium in the pig-iron. This is probably present partly as carbide and partly as cyanonitride. Although in the blast-furnace titanium nitride is sometimes formed, it is not present in the titanium-carbide alloy used in treating steel, for at the temperature of the electric-arc furnace, in which this alloy is made, with a reducing atmosphere and excess carbon the nitride is dissociated in favour of the carbide.

For general effectiveness titanium is the best of the various deoxidisers for steel. The carbide gives results quite as good as the pure metal and is much cheaper. A material is sold at 8 cents per pound containing 15 to 20 per cent Ti, and known as "Ferro Carbon Titanium." It consists of microscopic particles of titanium carbide held in a matrix similar to grey cast iron. When added to melted steel the matrix dissolves quickly, and the particles of titanium carbide are rapidly diffused through the bath, where they react vigorously on the oxygen.

The aluminothermic alloy, which contains very little carbon, is an alloy of aluminium and titanium in iron, and hence its use involves the production of the effects of both these elements. The chief objection to its use is the harmful effect of aluminium in hindering the removal of oxide and slag enclosures.

Titanium oxide acts as a flux for silicates and other slags that may be in the steel. The best cleansing action is obtained when the titanium is added without aluminium, or in the form of the carbide rather than as the aluminothermic alloy. The latter should only be used in the few rare cases where the addition of the carbon of the alloy would be undesirable. In soft steels the increase in carbon from this addition would not be more than about 0.01 per cent, so that the cases where this would make any material difference are very few indeed. Practically all the titanium used in steel in America at the present time is in the form of ferro-carbon titanium, a large percentage being used for rail steel, although its use in other steels is growing steadily.

"Titanium steel," properly speaking, is not made commercially at present. Such a title naturally implies a steel whose properties are dependent to an appreciable extent on a certain content of titanium. The advantages of the titanium-treated steels as made to-day are due to greater soundness, cleanness, and less segregation, and not, as

far as is known at present, to the small amount of titanium left in the metal. In no case has over 0.025 per cent of titanium been found in any sample of titanium-treated steel analysed at our laboratories. It is very difficult to make steel absorb more than 0.025 per cent titanium under the usual conditions of manufacture, and no use has yet been found for steel containing larger quantities that would warrant the attempt to produce commercially a real "titanium steel."

Steels made by the Bessemer, open-hearth, or crucible processes are treated with titanium, but most of this element is used in open-hearth steel. The alloy is furnished in various sizes, from lumps of about 1 in. diameter to powder, according to the quantity of steel to be treated at one time, and for the best results it must be added to the melted steel as it flows from the furnace to the ladle. After the addition the steel must be kept in the ladle for from three to ten minutes, depending on the size of alloy used and the mass of steel treated. Then the steel is teemed as usual into moulds where no further additions should be made. The amount of alloy recommended for use in rail steel is 13 lbs. per ton, which means an addition of 0.1 per cent of metallic titanium. A higher grade alloy is not used because its rate of solution in the melted steel is slower. The price of rails treated in this way is increased about 5 per cent. For castings and soft steels a smaller amount of alloy may be added. Low-carbon steels always contain blowholes even if treated with titanium, but the steel being normally cleansed by the titanic oxide, they are free from slag and are closed up when the ingots are worked. If they become oxidised, however, or contain slag, they will open up as seams or remain as slag inclusions in the metal. It is well known that if steel is completely deoxidised and no blowholes are formed, a large shrinkage cavity, or "pipe," will form in the centre of the upper part of the ingot. Titanium may cause piping, as well as other deoxidisers, but by properly designing the moulds piping may be controlled so as not to give much trouble.

The dependence of segregation on deoxidation is less obvious than that of soundness. Primarily, segregation is due to selective freezing. The freezing-point diagram of the iron carbon alloys shows that with ordinary steel the first metal to freeze is of lower carbon content than the remaining liquid, and the last liquid to freeze is of higher carbon content than the already frozen solid. But with well-deoxidised steel this selective freezing takes place in a quiet mass of pasty material, and the higher-carbon liquid is so intricately entangled in the lower-carbon solid that it does not have a chance to gather in the centre of the ingot to any great extent, and is finally frozen together with the lower-carbon material. If this steel is not well deoxidised, but gives off gas during solidification the gas rises and opens up passages through the steel, taking with it a little of the higher carbon liquid towards the top and centre of the ingot and leaving the solid lower-carbon material behind. This action will result in the formation of a large body of higher-carbon material in the upper part of the ingot, or, in other words, there will be excessive segregation. Phosphorus is subject to this action in the same way as carbon, and sulphur, existing in the steel as small non-metallic globules composed of a mixture of iron and manganese sulphides with a freezing point not much, if any, higher than that of the metal, is even more affected. For this explanation of the relation between segregation and oxides in steel the writer is indebted to Mr. N. Petinot, metallurgist of the Titanium Alloy Manufacturing Co.

Aluminium and probably also vanadium and silicon have an effect on segregation similar to that of titanium, but with vanadium the cost would be higher, and with silicon and aluminium impurities would be added to the steel. In most rail steel that has been properly treated with titanium, very small angular pink inclusions can be found with the microscope. These are titanium nitride, possibly contaminated with carbide. An average of many nitrogen

determinations on titanium-treated rails shows a distinctly lower amount present in solution in the metal than in untreated rails. If it is assumed that nitrogen has an injurious effect on steel, the lower amount must be an advantage, for even if the whole amount removed from the metal itself is still present in the pink inclusions, it could have no more ill effects in this form than any other non-metallic inclusions of the same size. As the titanium nitride inclusions are never found segregated in groups or streaks, like alumina and silicates, but are always very small and thinly scattered, their weakening effect on the metal is practically negligible. They have been found in titanium-treated steel axles as well as rails, but not in steel castings or soft steels where smaller amounts of titanium have been used.

Some so-called "titanium-treated" steels have not been any better in regard to segregation than the average untreated steel. These have constituted, however, an insignificant percentage of the total number examined in these laboratories. In every case these segregated "treated" rails have not shown a titanium content of over 0.005 per cent (while the average treated rails are well above that figure), and the pink nitride inclusions have also been absent. These facts indicate that not enough titanium was added to produce the usual effects. In the case of deoxidation of steel with titanium an excess of probably at least 0.005 per cent is necessary.

Forty-two samples of plain and treated open-hearth steel rails have been exhaustively tested, physically and chemically, in these laboratories.

The samples have all been taken from the "A rails" or first rails rolled from the ingots, after the usual discards from their tops, thus representing in each case metal from the top part of an ingot, which would show the greatest amount of segregation and impurities. The samples were always taken in pairs, one treated and one untreated from each rolling, so that in the final comparison the influence of the conditions of manufacture could be as far as possible eliminated. The final averages of the results are here tabulated.

Chemical analyses were made at four places on each rail—at top of head, centre of head, web, and flange. The lowest and highest figures for each rail were averaged together, giving the average low and high results:

	Untreated rail.		Treated rail	
	Low.	High.	Low.	High.
Carbon	0.58	0.82	0.63	0.76
Manganese	0.71	0.78	0.75	0.79
Phosphorus	0.016	0.026	0.018	0.023
Sulphur	0.032	0.058	0.031	0.040
Silicon	0.117	0.131	0.090	0.099

The following figures relate to tests on the head of the rails:

	Untreated rails.		Treated rails.	
Elastic limit	56,071		59,738	
Ultimate strength	118,138		124,857	
Elongation	12.8 p.c.		13.1 p.c.	
Reduction of area	14.3	"	15.4	"
Brinell hardness	220		226	
Impact resistance (Fre-				
mont machine)	1.47		1.58	
Endurance (a)	1312		1280	
Endurance (b)	16,550.920		23,923.628	

(a) By Landgraf-Truner machine. Alternate bendings endured before fracture.

(b) By White-Souther machine. Revolutions before fracture.

The improvements in other rails, from lower positions in the ingot, would be much less marked, but the rails that give most of the trouble in service are the segregated "A" rails, and these are rendered practically uniform and homogeneous as the other rails by treatment with titanium. Titanium-treated rails are not

better probably than the best possible untreated rail, but by this treatment the general standard of quality is unquestionably raised, uniformity is more nearly attained, and the bad heats of dangerously segregated or dirty steel are avoided.

To acquire still more positive data on the effect of titanium on segregation in rails, 79 "A" rails from different untreated heats and 31 similar rails from different treated heats were examined recently by means of sulphur prints and chemical analyses for carbon made on each at an upper corner of the head and at the junction of head and web. The average difference between these two points was 17 per cent for the untreated rails, and the worst rail showed 40, while only 29 of these 79 rails showed less than 12 per cent. For the treated rails the average difference was 3.1 per cent, and the worst one gave 11.5 per cent, none of the 31 showing over this amount.

The railroads have been acquiring data for some time in regard to the wear of titanium-treated rails in track as compared with that of ordinary open-hearth rails. The results have been uniformly favourable to the treated rails, in some cases very decidedly so. For instance, on a sharp curve on the Boston Elevated Railway titanium-treated rails laid alternately with plain rails of practically the same composition showed 41 per cent less wear after 214 days' service. In a test made by the Rock Island Railroad titanium-treated rails in seventeen months had 0.014 sq. in. abraded from their sections on the average, while electric steel rails showed under the same conditions a loss of 0.058 sq. in. and ordinary rails 0.075 sq. in.

In axle steel it has been found similarly advantageous to use titanium for purifying the metal and preventing segregation. In steel castings the use of titanium as a deoxidiser has usually been successful and satisfactory, and in soft steel for plates and thin sheets much titanium is used. This element is preferred to any other deoxidisers because it does not leave any product of its oxidation in the steel, as aluminium and silicon do, and the ingots therefore roll out smoother and the finished sheets have a better surface. Small defects on the surface of a sheet are very serious in galvanising, so that the smoother surface of titanium-treated sheets, due to cleaner ingots, is much appreciated.—*Chemical Engineer*, xxi., No. 5.

THE INCLUSION OF ELECTROLYTE BY THE DEPOSIT IN THE SILVER VOLTAMETER.*

By T. W. RICHARDS and F. O. ANDEREGG.

(Concluded from p. 149).

III. Inclusions Determined by Analysis.

(NOTE.—This method was tried once before at Harvard, the analyses having been made by Mr. E. Collins near the beginning of his part in the research (*Proc. Am. Acad.*, 1899, xxxv., 139). No claim was then made for great accuracy, but the outcome was in favour of a slight inclusion. The cause of the errors in Experiments 35 and 36 noted by Rosa (*Bur. Standards*, 1914, *Bull.* x., 518) cannot now be traced, as the original notes are no longer accessible. In any case, the older the analyses do not compare in authority with those given below).

After a regular double electrolysis (with two coulometers in series) had been made, the crucibles containing the weighed deposits were placed in large covered beakers nearly filled with warm water, and a slight excess of re-distilled nitric acid was added. When the silver had been completely dissolved, the solution was quantitatively transferred to a 2-litre precipitating flask. To the large bulk of solution an excess of very pure hydrochloric acid was gradually added—enough to precipitate all the silver—leaving dissolved an excess of ionised chlorine, in

hundredth normal concentration. (Forbes, *Journ. Am. Chem. Soc.*, 1911, xxxiii., 1937, has shown that silver chloride is least soluble in such a concentration of chloride ions. Calculating from the solubility product, 2×10^{-10} , it would take 5 litres of solution to dissolve 0.01 mgrm. of silver chloride, and hence no correction need be applied).

The precipitate was agitated till it had thoroughly coagulated, and allowed to stand in a dark room for twenty-four hours with occasional shaking; the filtering was done through a tared Gooch-Monroe crucible. The precipitate was washed ten times with wash-water containing hundredth normal hydrochloric acid, being transferred to the crucible with the same wash-water, and finally dried for five hours at 180° to 190° , cooled, and weighed. The bulk of precipitate was then placed in a previously ignited porcelain crucible, and after weighing the silver chloride was fused in a porcelain air-bath. The fused mass was nearly colourless in all cases. Except silver chloride, the only substances present in this analysis are volatile, hence the process is an unusually precise one. A trace of silver chloride remaining in the precipitating flask was dissolved in a little ammonia, determined in the nephelometer, and added to the main weight.

The vacuum corrections for metal and halide are respectively, -0.031 mgrm. and $+0.071$ mgrm. per grm. These were duly applied, and the calculation was carried out on the assumption that the atomic weights of the two elements are respectively 107.880 and 35.459. The results are given in Table I.; the table is easily comprehensible. For each of the last two analyses the products of the two coulometers were united for analysis. The calculated figures in the last column make allowance for the fact that the included mother-liquor must have contained about 8 or 10 per cent of silver nitrate, the silver in which must have been precipitated as chloride and weighed with that coming from the electrolytic metal.

TABLE I.—Analysis of Electrolytic Silver Dried at 160° .

No. of Expt.	Corrected wt. Ag. Grms.	Corrected wt. AgCl. Grms.	Calculated wt. AgCl. Grms.	Diff. Mgrms.	Diff. in per cent.	Inclusions corrected for Ag as AgNO ₃ . Per cent.
20	2.79247	3.70988	3.71033	0.45	0.0121	0.0128
21	3.25640	4.32631	4.32674	0.43	0.0100	0.0106
	3.25644	4.32637	4.32680	0.43	0.0100	0.0106
22	2.66857	3.54521	3.54570	0.49	0.0138	0.0144
	2.66859	3.54531	3.54573	0.42	0.0118	0.0125
23	5.92000	7.86453	7.86585	1.32	0.0167	0.0176
24	5.72318	7.60322	7.604335	1.115	0.0147	0.0155

Total 26.28565 34.92083 34.925485 4.655 0.0133 0.0141*

* If Cl = 35.460, this value would be 0.0148 per cent.

Evidently the actual weight of silver chloride found was always less than the theoretical weight. Hence the silver contained included impurity.

The quantity of inclusion thus found by direct analysis (0.014 per cent) is close to that found by Richards and Heimrod, 0.018 (*loc. cit.*, p. 435). The present series of analyses determines this quantity by a method quite different from the old way.

In order to forestall the criticism that the deficiency thus found might simply be due to loss of silver during the analysis, very pure fused silver was prepared and analysed with exactly the same precautions.

TABLE II.—Analysis of Pure Fused Silver.

Corrected wt. Ag. Grms.	Corrected wt. AgCl found. Grms.	Calculated wt. AgCl. Grms.	Diff. Mgrms.	Diff. in per cent.
6.22211	8.26738	8.26725	+0.13	+0.002
5.16568	6.86361	6.86359	+0.02	0.000
5.18476	6.88875	6.88893	-0.17	-0.002
16.57255	22.01975	22.01977	-0.02	0.000

* *Journal of the American Chemical Society*, xxxvii., No. 1.

The result is very different from that previously found in the case of the crystallised electrolytic silver, and corresponds exactly with the value 35.459 for chlorine. The international value 35.460, also, is within the limit of experimental error. The evidence is very strong, therefore, that the analytical procedure was correct, and hence that the electrolytic silver prepared as we had prepared it, contains more than one part in ten thousand of included mother-liquor.

IV. Inclusions Determined by Heating the Deposits in the Cathode Crucible.

The ignition of the deposit for the purpose of determining the inclusions by loss of weight has been often used in the past, first by Lord Rayleigh and Mrs. Sidgwick, and later by many others. Some, trying to use it, have failed to heat the silver hot enough, as already stated.

In our experiments, after the crucible with its deposit had been washed, dried, and weighed as usual, it was placed on a quartz triangle in a dark room. A clean porcelain crucible was inserted into the mouth to protect the material from dust, and to cool and catch traces of silver vapour. The platinum was heated very carefully, with a burner held in the hand, until it attained dull redness, just barely perceptible in the dark. Great care was used to not exceed this temperature, and to heat the crucibles all over, as evenly as possible. The crucible was then cooled, and weighed once more.

Such heating slightly alloys the two metals; on dissolving the silver in nitric acid a perceptible amount of platinum remained. In preparation for a new trial the inner surface was afterwards scrubbed, washing finally with acid and water. The crucibles lost a few tenths of a mgrm. each time, due to the removal of the platinum. Burnished crucibles suffered much less than those roughened by continuous use. This complication, of course, had not the slightest effect upon the quantitative experiment.

To settle the question raised by Jaeger and von Steinwehr, as to whether a platinum crucible alone loses weight when heated, one of ours was heated five times, just as if it had contained silver. The total loss was only 0.05 mgrm., or 0.01 mgrm. for each heating. This is negligible, but the corresponding correction was applied to each result for the sake of completeness.

The results concerning the amounts of included electrolyte found by heating the precipitated silver are summarised in Table III. Each figure is calculated from the actual loss on heating by adding to that quantity 6 per cent of its value, to allow for the silver which must have remained from the included nitrate decomposed by heat. This will be explained more fully later. The first column records the amount of inclusion in silver precipitated on a crucible which had been somewhat scratched and roughened by van Dijk's process of mechanical

removal of previous precipitates; the second column records the result for freshly burnished crucibles (both used as porous-cup coulometers); the third column gives the amount in an instrument according to Kohlrausch (the first four results coming from burnished crucibles, and the last three from rough ones); the fourth column shows the increased inclusion when some of the anolyte is permitted to come into contact with the cathode deposit, and the last column shows the greatly increased effect when a large surface receives the silver crystals. The deposit varied in weight from 1.9 to 3.1 grms. In order to be sure that no silver volatilised during the ignition, the porcelain crucible which had been used as a cover during all the heatings was warmed with nitric acid; but no silver was found in this liquid on testing in the nephelometer.

These results are worthy of careful study.

In the first place, one notes that the average of the first column, including all the results obtained with the ordinary somewhat roughened porous cup voltameter, is 0.015—a figure close to that found by the actual analysis of the silver, 0.014, recorded in the last section, as well as to the earlier results found at Harvard and the still earlier work of Lord Rayleigh.

In the next place, it is clear that a roughened crucible considerably increases the inclusion, its figure being 0.015 instead of 0.010 found in the case of a burnished crucible.

Again, it is apparent from Column 5 that, other things being equal, the inclusion is approximately proportional to the surface on which the silver is deposited—for the large platinum beaker-crucible used in this series had about twice the surface of the smaller vessel used for the experiments in Column 1, and the inclusion was about double. This surface effect is doubtless the real cause of the so-called "volume effect" noticed by various other experimenters (see, for example, Rosa, *Bull. Bur. Standards* ix., 514, 1913), for they failed to observe and correct for this greater occlusion which occurs on a larger surface. These figures give striking evidence of the importance of determining the amount of inclusion in each case, and by their final consistency strongly support the other work.

The surface effect, producing greater inclusion, is doubtless also the reason why the Kohlrausch form of voltameter gave a lesser deposit; for in this form the receptacle placed under the anode to receive the "anode slime" cuts off nearly half of the cathode from usefulness, and the silver is actually deposited upon only a part of the platinum surface which would be available in the porous-cup voltameter. This, of course, by increasing the current density, diminishes the practical maximum current strength which the instrument can safely endure, and makes a large crucible no more efficient than a small one would be with the porous cup.

Finally, it is evident from Column 4 that the anode impurities promote the inclusion, in confirmation of the Harvard work of 1900–1902 and of Hulett's later results.

Because, also, as the work at the Bureau of Standards has shown, by very extended experiments, both current density and temperature affect the size and distribution of the crystals, these factors also must affect the inclusion.

Evidently it is impossible to apply a correction so variable to any work upon this subject, either one's own or that of others, without an intimate knowledge of every detail. The only satisfactory method is to determine with due precaution the amount of included electrolyte in every crystalline precipitate, and no work in which this has not been done can possess final authority, at least as regards the exact weight of the precipitate.

V. The Nature and Distribution of the Inclusion.

It is, of course, possible that the mother-liquor included in the crystals is not of exactly the same composition as the original electrolyte. Around the cathode during active electrolysis the solution of silver nitrate is necessarily diluted, and the solution may be caught and imprisoned in this diluted condition.

TABLE III.—Inclusions in Precipitated Silver, found by Heating.

(Expressed in fractions of per cent of weight of silver).

Porous cup roughened crucible.	Porous cup burnished crucible.	Kohlrausch form.	Cathode less protected from anode.	Porous cup, large cathode vessel (roughened).
0.0155	0.0076	0.0072	0.0218	0.0352
0.0134	0.0108	0.0061	0.0224	0.0311
0.0174	0.0097	0.0039	—	—
0.0194	0.0100	0.0115	—	—
0.0171	0.0100	0.0045	—	—
0.0174	0.0119	0.0055	—	—
0.0178	—	0.0115	—	—
0.0125	—	—	—	—
0.0107	—	—	—	—
0.0139	—	—	—	—
Av. 0.0155	0.0100	0.0083	0.0221	0.0332

A moment's thought will show, however, that the exact concentration of the imprisoned mother-liquor is not a serious question. For example, if the total inclusion is 0.015 per cent, a knowledge of the composition of the mother-liquor within 7 per cent would correspond to an accuracy of 1 part in 100,000 of the crystallised silver. This is a high degree of accuracy, which rarely needs to be exceeded. Supposing, therefore, that one starts with a 10 per cent solution of silver nitrate, more than half of the dissolved substance might be eliminated without causing a serious effect upon the result. The error from any possible change of concentration is therefore less than the possible error which might be caused by scraping the crystals from the dish; for this process (as will be shown) allows water to evaporate from cells opened by abrasion. *The really important point, as usual, is to determine the amount of included water.*

On this account we have made no search as to the exact composition of the included mother-liquor. The analyses made by Hulett seem to be more than sufficient for the purpose. Although variable, they indicate that the enclosed liquid under the conditions involved does not lose anything like as much as half of its dissolved salt.

As already stated, the presence of carbon dioxide, found by Hulett in the gases obtained from the silver, is probably to be ascribed to dust, which doubtless furthers occlusion of mother-liquor. No other reasonable source is assignable. At a high temperature this dust, even if protected from air, would burn in the oxygen of the nitric acid and be expelled. Obviously, therefore, the carbon would be eliminated from the final result, whether its weight were calculated from the amount found as a gas or simply from the loss of weight of the heated silver. It is almost impossible to exclude such minute traces of dust under ordinary conditions; therefore it is comforting to feel that in this case, at least, their influence is negligible.

One mgrm. of the original 10 per cent electrolyte leaves 0.063 mgrm. of silver on ignition, and 8 per cent solution would leave 0.051 mgrm. The cathode occlusions are probably between these limits, which are close enough for the purpose. Hence, to obtain the exact weight of the silver deposited electrolytically as metal, one must subtract from the weight of the precipitate ignited at a dull red heat about 6 per cent of the loss on heating, as has been done above. As already stated, this is quite accurate enough. Incidentally, it may be stated, that a similar correction was thus applied in the early Harvard investigations (*Proc. Am. Acad.*, 1902, xxxvii., 421; *Zeit. Phys. Chem.*, 1902, xli., 308). For most purposes, where the weightings are not carried beyond 0.1 mgrm. the correction may be neglected altogether; the weight of the silver crystals heated to incipient redness may be taken directly as the weight of the metallic silver precipitated by the electrolysis.

The question concerning the distribution of the inclusion in the deposit is of more importance. Is the imprisoned liquid wholly in the body of the crystals, or is part of it held between the crystals and the platinum cathode? If the latter is the case, van Dijk's and Hulett's method of removing the crystals from the dish may open a part of the cells, allowing some of the liquid to evaporate; thus both the weight and concentration of the included solution may be wrongly estimated. This is a matter easily susceptible of experimental decision, and our study of it is recounted below.

In the first place, a number of deposits were prepared with the purest electrolyte and all the precautions already described. After most carefully washing, weighing, and drying the deposit, each deposit was removed as far as possible from the platinum cathode with a platinum spatula. Both dish and spatula suffered somewhat, and the detached crystals of silver contained some platinum; but this did not affect the main point in question. The crystals were placed in a test-tube, and washed with a little water, which was then filtered through a Gooch crucible provided with quantitative asbestos. The cathode crucible was similarly washed, and its wash water

similarly filtered. These wash waters were tested in the nephelometer by comparison with standard silver nitrate solution with every precaution.

Table IV. summarises the results obtained with crystals deposited on cathodes somewhat roughened by this drastic treatment.

TABLE IV.—*Silver Nitrate contained in the Wash Water from the Crucibles and Crystals.*

No. of Expt.	Deposit Ag in grms.	On crucible. Mgrm.	On crystals. Mgrm.	Total Mgrm.	AgNO ₃ . Per cent
13	2.91711	0.025	0.037	0.062	0.0021
	3.00918	0.023	0.031	0.054	0.0018
14	2.73102	0.025	0.030	0.055	0.0020
	2.73097	0.028	0.024	0.052	0.0019
15	2.43529	0.011	0.018	0.029	0.0012
	2.43523	0.017	0.014	0.031	0.0013
16	3.19442	0.014	0.016	0.030	0.0009
	3.19439	0.026	0.012	0.038	0.0012
Total	22.64761	0.169	0.182	0.351	0.00155

Thus, on the average, every grm. of silver precipitated in this way enclosed 0.015 mgrm. of silver nitrate between the crystals and the dish. It remained to discover the amount of mother-liquor imprisoned within the crystals themselves.

After drying these washed crystals for at least an hour at 160°, they were placed in a quartz crucible provided with a cover of the same material. When carefully weighed, they were heated in the flame of a Bunsen burner to dull redness. This heating was usually accompanied by a crackling sound, as the enclosed substances made their escape. The cooled crucible was weighed, and again heated, cooled, and weighed as before until constant weight had been obtained.

The values obtained by this method gave a measure of the volatile matter in the crystals, which must be corrected for residual silver as before. In four determinations, 7.22 grms. of silver lost 1.23 mgrms., or 0.017 per cent. Corrected for residual silver from the enclosed nitrate, this becomes 0.018 per cent.

Because of a fear lest some silver might have been lost by volatilisation from the quartz crucible, the test was repeated, with a quartz test-tube, 15 cm. long, in place of the crucible. In this test-tube there were heated two portions of crystals which had been accumulated from several electrolyses, scraped from the crucibles and afterwards washed as before. To ensure precision in weighing, a tare was used, consisting of a similar amount of silver which had already been heated in the crucible. A small tube of radio-active substance was kept in the balance case to remove any electrostatic charges from the tubes, and every precaution was taken to ensure accuracy. During the ignition a thin walled, cone-shaped glass tube was inserted well down into the top of the quartz tube, which was then inclined at an angle of 30° to 45° with the horizontal, and heated in a Bunsen flame. From this arrangement no trace of silver vapour could escape during the ignition. The inner glass tube was duly tested for volatilised silver by treatment with nitric acid. In one case a trace was found, and due correction applied. In the second trial none was found.

When the silver had reached constant weight on successive treatings, the tube was evacuated with a water-pump, and again heated to see what effect the absence of most of the oxygen would have. Von Wartenburg (*Zeit. Elektrochem.*, 1913, xix., 482) suggests the formation of silver oxide at high temperatures to explain the fact that silver is more volatile in oxygen than in an atmosphere of nitrogen or in a vacuum. The heating in the partial vacuum produced no perceptible effect on the weight. Two trials were made, using 10.1 and 9.8 grms. of crystallised silver, respectively. The corrected losses of weight were 1.37 mgrms. and 1.12 mgrms. (or 0.0135 and 0.0115 per cent), respectively. Averaging the results, we see

that these specimens of washed silver contained 0.0125 per cent of mother-liquor. To this must be added the amount of silver nitrate which had been washed from their abraded surfaces, namely, 0.00155 (see Table IV.), making 0.014 per cent in all. This is somewhat less than the loss of weight found in similar deposits when the crystals have not been removed from the dish (see Table III.); hence it would appear that the removal of the crystals opens some cells which otherwise would remain closed at 160°, and allows the water to evaporate from the previously imprisoned silver nitrate. Hence it is clear that the method of van Dijk and Hulett is probably not an adequate way of determining the actual total amount of included mother-liquor which is weighed with the crystals while the latter are still adhering to the dish.

Another very strong piece of evidence in support of these conclusions about the included mother-liquor is to be found in the comparison of the final weights, after ignition, of deposits upon large and small coulometers in the same circuit. Whereas before heating the two gave very different results, after heating they were almost identical.

TABLE V.—Weight of Deposits in Large and Small Porous-cup Coulometers.

First Expt.	Weight after drying at 160°.	Weight after ignition at dull redness.	Final weight after cor. for residual Ag from AgNO ₃ .	Weight of included electrolyte.
Large coulometer	1.89559	1.89494	1.89490	0.00069
Small coulometer	1.89535	1.89492	1.89490	0.00035
Difference	0.00024	0.00002	0.00000	0.00034
Second Expt.				
Large coulometer	3.13902	3.13812	3.13807	0.00095
Small coulometer	3.13868	3.13808	3.13805	0.00063
Difference	0.00034	0.00004	0.00002	0.00032

The second and third columns of figures show how nearly alike the results are after the ignition; that is to say, the apparently large difference between the results of the two sizes of coulometers (which would have been left unexplained as a "volume effect" if the methods of the three national bureaus had been used) is annihilated by the simple device of heating the crystals to a temperature high enough to drive off the included water.

In a recent able article by Bates and Vinal appears the following statement (*Journ. Am. Chem. Soc.*, 1914, xxxvi., 932):—"The whole question of inclusions has been critically discussed by Rosa, Vinal, and McDaniel (*Bur. Standards*, 1914, *Bull.* x., 516). Their opinion is that the deposits so perfectly crystalline as those formed from the purest silver nitrate do not contain significant inclusions."

(NOTE.—The main quantitative evidence depended upon a single experiment (p. 522), in the interpretation of which the erroneous assumption was tacitly made that inclusion does not exist in the porous-cup voltameter and is the only error in the filter paper voltameter. The fallacy will be explained more clearly in the next paper upon the topic, to appear shortly.)

To us it seems that any such superficial evidence is far from convincing. One of us has shown repeatedly (*Proc. Am. Phil. Soc.*, 1913, xlii., 28; *Journ. Am. Chem. Soc.*, 1911, xxxiii., 885) that no matter how beautiful a crystal, or how perfectly crystalline and transparent its structure may be, yet when it is crystallised from aqueous solution it is almost, if not quite, certain to contain some of the mother liquor, either in accidental sub microscopic cells or in "solid solution." Indeed, a careful review of this latest published comment, in the light of the foregoing experiments, fails to reveal any adequate argument against our conclusion.

VI. The Purity of the Ignited Deposit.

Only one final question remained:—Is crystallised silver, which has been thus heated at a dull red heat, really pure silver? Upon this point the validity of the whole coulometric process depends. From the fact that the amount of inclusion as found by analysis agreed closely with that found by heating the silver, it is clear that the heated crystals must have been very nearly pure; but the matter was clinched by actual analyses of two of the specimens remaining from the work described above. On solution in nitric acid, each preparation was filtered through a Gooch-Munroe crucible with every quantitative precaution, and the residual platinum derived from the cathode was carefully weighed. The analysis of the solution was conducted by precipitation with pure hydrochloric acid exactly as in Section III.

TABLE VI.—Analyses of Ignited Crystallised Silver.

Weight Ag + Pt vac.	Weight Pt.	Weight Ag.	Cor. weight fused AgCl vac.	AgCl calc.	Deficiency. Mgm.
5.94112	0.01533	5.92279	7.86933	7.86938	0.05
5.01725	0.01020	5.00706	6.65256	6.65262	0.06
Total			14.52189	14.52200	0.11

The conclusion is, therefore, that such finely crystallised electrolysed silver, which has been ignited at a dull red heat, contains less than 0.001 per cent of impurity. Except for the difficulty of removing the silver from the cathode, and from the clinging contamination of platinum therefrom, this would be a good method of making very pure metal. Possibly the fine crystals precipitated in an electrolytic silver-tree, or by formate, would, on gentle ignition, show equal purity; if so, either of these very obvious processes would be extremely convenient for the preparation of this substance for many quantitative purposes.

In a recent paper Bates and Vinal (*Journ. Am. Chem. Soc.*, 1914, xxxvi., 916) have compared in a very interesting way the iodine coulometer of Washburn with the silver coulometer. Deviations among the results were noticed, but no satisfactory explanation of them was given. When, however, it is remembered that the investigations made no allowance whatever for included mother-liquor, and when one studies the tables on the foregoing pages in this paper, the reasons for the deviations become manifest. With the porous-cup voltameter the inclusion is greatest on the largest surface; hence such deposits were the heaviest, as they found. The Kohlrausch form (Smith's large new form is a modification of the Kohlrausch arrangement), because it restricted the surface of the large vessel, would be expected to yield a result between the two; moreover, the error due to anolyte, to be discussed in a subsequent paper, may enter into its results, as well as into those from very diminutive coulometers. The exact correction of these results for inclusions is unfortunately impossible, because the inclusion varies with the extent and roughness of the surface of the cathode. But an approximation may be made if we assume the 120 cc. porous-cup voltameter (which gives the lowest results) as a standard, and then correct its indications by applying the average correction which we have found in this present work (0.015 per cent). This would, of course, raise the calculated atomic weight of iodine by this percentage, if silver is assumed as the standard. Taking silver as 107.88, iodine was found to be 126.898 by Vinal and Bates with the small porous-cup instrument; but corrected for inclusions in the silver this becomes 126.917. This corrected value is in much better agreement with Baxter's best result, 126.932, than before. The remainder of the difference may perhaps be ascribed either to the need of a larger correction for inclusions, or possibly to the existence of a trace of chloride of iodine in the iodine used by Bates and Vinal for standardisation. The latter's result is almost identical with Baxter's preliminary value,

126.916. (Bates and Vinal took great pains in the purification, but not so much as Baxter; see Baxter, *Journ. Am. Chem. Soc.*, 1910, xxvii., 1591; also *Proc. Am. Acad.*, 1904, xl., 419).

The assumed international value of the Faraday is also, of course, affected to an equal extent by inclusion. If, as we cannot but believe, the 1.11800 mgrms. of silver supposed to be deposited by a coulomb contained inclusions, the true value may well be nearer 1.1179. It is profoundly to be regretted that all the able recent experimenters on this absolute value seem to have entirely overlooked the importance of this matter.

We are much indebted to the Carnegie Institution of Washington for apparatus used in this research.

Summary.

In confirmation of earlier work by Lord Rayleigh and that at Harvard, as well as of the subsequent work of Hallett, the presence of included electrolyte in the crystallised silver deposited in a silver coulometer (voltameter) has been shown in the following ways:—

First, by quantitative analysis of the crystals after drying to constant weight at 165°.

Secondly, by ignition of the crystals on the cathode at a dull red heat.

Thirdly, by ignition of the crystals, separated from the cathode, in a quartz test-tube, arranged so as to prevent evaporation of silver.

Fourthly, by showing that simultaneous deposits which were unequal in weight before ignition had attained equality after ignition.

The included mother-liquor was shown by quantitative experiments to be partly within the crystals, and partly between the crystals and the walls of the cathode.

The quantity of the inclusion varies, increasing (as would be expected from the immediately foregoing statement) with increasing surface and with increasing roughness of the cathode. It may vary from 0.004 to 0.035 per cent of the weight of the silver. The silver remaining after the ignition was shown to possess a very high degree of purity, and at incipient redness it was shown to be essentially non volatile during brief treatment.

The experiments of the three national bureaus of America, England, and Germany, while illuminating in many respects, failed to throw light on the matter, because of incomplete experimentation. Either the temperature of ignition was inadequate, or some other oversight intervened—as, for example, in the attempt to dissolve the precipitated metal in fifty times its weight of mercury when 2500 times its weight are really needed for complete solution.

Because of the variation of the amount of inclusion according to circumstances, it is unfortunately impossible to correct older results. But there seems to be no question that correction is necessary, especially in the case of the large dishes used by Smith, Mather, and Lowry. Hence, much of the work should be repeated. The correction affects the value of the electrochemical equivalent, the Faraday, the value assigned to the Standard Weston cell, and all ratios of atomic weights determined electrically; hence, it is a question of importance.

NOTICES OF BOOKS.

The Rare Earth Industry. By SYDNEY J. JOHNSTONE, B.Sc. (London). London: Crosby Lockwood and Son. 1915.

The applications of the rare earths are continually increasing in number and importance, and there is room for a book such as this dealing with the subject from a practical point of view. Tantalum, tungsten, uranium, and vanadium are included, and the extraction of the metals and the industrial uses to which they and their derivatives are put are shortly described. The chapter on the thorium and cerium industries deals with the manufacture of in-

candescent mantles and pyrophoric alloys, and the incandescent electric glow-lamp industry is also given special consideration. The descriptions of methods of preparation, analysis, &c., are somewhat condensed, but the references to foreign and English literature are very full and have been carefully compiled. In the chapter on the radio-active industry, which is contributed by Dr. Alexander S. Russell, a clear little theoretical summary of the development of the subject is given, and methods of separating and testing radio active bodies are described in outline.

The Gas Chemists' Summary, 1914. By A. V. HENDRICKSON. London: Walter King. 1915.

THIS book is a well arranged compilation of information relating to gas works chemistry, in which the literature which has been published during the year is carefully reviewed. No important papers or articles seem to have been overlooked, and gas works chemists who wish to keep their knowledge up to date will find the book a very valuable aid. The bibliography includes nearly 150 references, and the articles have been well and accurately summarised.

Erreur de la Thermodynamique. ("Error of Thermodynamics"). By EMILE-LOUIS MARIS. Paris: Imprimerie Polyglotte Hugonis. 1915.

NOBODY will be found to combat the assertion of the author of this pamphlet that the recognition of error is the urgent duty of science at all times and the necessary prelude to progress, but his subsequent dogmatic statements, unsupported by rational argument, will not win him many adherents. His main contention is that the whole theory of thermodynamics is based upon an error, which bars the way to the acquisition of true knowledge, but he brings forward practically nothing in the way of proof of the truth of his contentions, and his criticisms of the work of the great investigators are quite unconvincing.

CORRESPONDENCE.

THE INSTITUTION OF CHEMICAL TECHNOLOGISTS.

To the Editor of the Chemical News.

SIR,—I have read with much interest the letter from Mr. Noel Cassal which appears in your issue of September 24, and, with your permission, I desire to state that I am in full agreement with the opinions expressed by him. I must in the first place commend the extreme moderation with which your correspondent has replied to Prof. Armstrong. The latter's reference to the Institution, if made in normal times, would be regrettable, but in existing circumstances is doubly so, since the present crisis imperatively calls for a true spirit of co-operation in all classes of the community. It is such a spirit in the chemical profession that the Institution wishes to establish. Consequently, instead of opposition it is deserving of every support, and should attract all who have at heart the interests of the profession. The principle recognised by the Institution is that it is only through the combined efforts of chemists themselves that it will be possible to bring home to the public the importance of chemistry to national prosperity. It is no exaggeration but the bare truth to say that upon the due appreciation by the nation of the value of applied chemistry the future success of our industries depends. Only through combination will chemists gain the respect of the public, and only when the public have come to respect the chemical profession will its value be recognised.

The policy of the Institution of Chemical Technologists requires no defence. It is not a destructive or negative policy; it is a positive and perfectly definite one. It aims at a united chemical profession and the acceptance of it at its proper valuation. At present the Institution is

fighting alone. It is the only body that has raised a protest against the degrading terms of service of chemists in Government employ and the invidious distinction made by the State between professional chemists and medical men. In respect to this "I could a tale unfold," but am in honour bound not to "reveal the secrets of the prison-house" until the conclusion of the war. Without doubt, chemists have themselves mainly to blame for the present condition of their profession, and they have yet to learn that only unity of purpose and professional federation will raise that profession to the position it is entitled to occupy. When they have learnt this lesson and have begun to give practical expression to their views, they will then be in a better position to teach a notoriously unscientific public the value of applied chemistry. This end will assuredly not be reached if the public are led to believe that the profession of chemistry is in the position of a house divided against itself.—I am, &c.,

J. WILBERFORCE GREEN,
Registrar, Institution of Chemical Technologists.

ESTIMATION OF SULPHUR IN GALENA.

To the Editor of the Chemical News.

SIR,—I have read with interest the letter on "The Estimation of Sulphur in Galena," by Mr. Owen Joseph, which appeared in the CHEMICAL NEWS of September 17.

It seems to me that the method as therein described cannot lay claim to a great measure of accuracy, for the sulphur estimated can only be that which is combined with the lead in the galena, whereas the chemist has to do with samples of galena containing more or less impurities in the form of sulphides of zinc, iron, antimony, &c.; the sulphur combined with these foreign metals remains in solution in the method given by Mr. Joseph.

I would suggest that the addition of a crystal or two of lead nitrate to the galena before dissolving would give more exact results, by providing the lead necessary to precipitate all the sulphur present in the ore.—I am, &c.,

W. T. PHILLIPS.

Santa Engracia, 8, Linares, Jaén, Spain,
September 27, 1915.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxi. No. 7, August 17, 1915.

Control Method for Ascertaining Rapidly the Quantity of Nickel Deposited on Nickeled Objects.—M. Pontio.—The method depends upon the combined action of hydrogen peroxide and mineral acids in contact with iron or copper. If an object nickeled by electrolysis is immersed in a cold solution of dilute hydrochloric acid and hydrogen peroxide the two following phenomena occur:—(i) A more or less rapid penetration of the oxidising mixture through the interstices of the deposit. The rapidity of the penetration is a function of the quantity of metal deposited and of the proximity of its molecules, and if the layer is thick and uniform it becomes effective only when the liquid has destroyed a part of the nickel and thus got through to the copper. (ii) A slow attack of the nickel in the cold, which facilitates the penetration of the oxidising mixture. If the metal underneath is copper and the layer of nickel is thin the formation of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ is instantaneous. If the nickel layer is sufficient (2–3 mgrms. per sq. cm.) $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ is also formed, and the formation of these salts (detected by their green coloration) is more rapid the thinner the layer of nickel. If the metal underneath is iron the appearance of iron perchloride is much more rapid than that of cupric chloride for an equal quantity of nickel. If the metal underneath is iron which has been coppered previously the copper appears instantaneously if the layer of nickel is thin, while if it is thick the iron appears at the

beginning of the reaction, followed by the appearance of the copper in a period of time which is proportional to the quantity of nickel deposited. The quantity of nickel necessary to produce a satisfactory layer varies with the nature of the underlying metal; it is much less for a fine-grained, compact, and homogeneous metal than if it has an irregular, granulated, fissured, or striated surface. The metals ought to be polished before being nickeled, and iron ought also to be ground. A layer of nickel amounting to 2 mgrm. per sq. cm. is enough to cover a copper object, but it ought to be increased to 4 mgrms. per sq. cm. for iron objects which have been previously coppered.

No. 8, August 23, 1915.

This number contains no chemical matter.

MISCELLANEOUS.

The Chemical Society.—The Council have arranged for three lectures to be delivered at the Ordinary Scientific Meetings during the coming session. The first of these lectures will be delivered on November 18 by Dr. E. J. Russell, who has chosen as his subject "The Principles of Crop Rotation." The titles of the two subsequent lectures—to be delivered on February 3 and May 18, 1916, by Prof. W. H. Bragg, F.R.S., and Prof. F. Gowland Hopkins, F.R.S., respectively—will be announced later. The Rooms of the Society will be open for informal meetings on October 21, 1915, and on January 13 and May 11, 1916, at 8 p.m., when the President and Council will be glad to receive Fellows. Smoking will be permitted and light refreshments provided. It is hoped that many Fellows will respond to the invitation of the Council to exhibit apparatus and specimens of interest, and to show experiments; those wishing to do so are requested to communicate with the Assistant Secretary not later than the Monday previous to the meeting.

A New Queensland Industry.—Eucalyptus Oil.—Eucalyptus oil is now being produced in Queensland, and the following description of the *modus operandi* is being circulated:—The cost of a plant for extracting eucalyptus oil varies greatly according to the method adopted. A common plan is to use two 400-gallon iron ships' tanks, the condensing being done in a long pipe laid in the bed of a creek. If sufficiently long the condensation is perfect. Such a plant would cost about £25. If a boiler is used to supply steam, and larger digesters are employed, then the cost would be proportionately greater; in fact a large plant might run into a considerable amount. This expenditure would only be warranted if the supply of the material were considerable. The wholesale value of the oil varies with its constituents, and many classes of oil are obtainable from the eucalyptus. The common peppermint oil, used for the separation of metallic sulphides, is worth about 6d. per lb. at the stills. The eucalyptus oils—those rich in eucalyptol and not containing phallandrene, and used for pharmaceutical purposes—are worth about 1s. per lb. at the still; the geranyl acetate oils, 10s. to 12s. per lb., and the other kinds at various prices. Since the war the demand for eucalyptus oils has fallen off. There should be a great demand for certain kinds of eucalyptus oils, and this will eventually be the case. The profit is largely governed by the law of supply and demand. The cost of production is made by cutting the leaves (an expensive item where labour is dear), carting to the still, fitting up the still, and leaves and firing. No particular skill is required to distil the oil, but it is necessary to know what material is obtainable from the species to be worked. Although it is now well known that each particular species yields an oil fairly constant in character, yet the products of species vary so much between themselves and the yields of oil are so variable that it is desirable to determine the species before work is done on it. The oils of about 160 species of eucalyptus have been determined in Queensland, so that the data are complete.

THE CHEMICAL NEWS.

VOL. CXII., No. 2916.

THE NEUTRAL AMMONIUM SALTS OF SOME SUBSTITUTED BENZOIC ACIDS.

(FIFTH COMMUNICATION).

By LEROY McMASTER and I. H. GODLOVE.

(For previous papers on this subject see *Am. Chem. Journ.*, 1913, xlix., 84; *CHEMICAL NEWS*, 1913, cviii., 136; *Am. Chem. Journ.*, 1913, xlix., 294; *CHEMICAL NEWS*, 1913, cviii., 182, 193; *Journ. Am. Chem. Soc.*, 1914, xxxvi., 742; *CHEMICAL NEWS*, 1914, cx., 212; *Journ. Am. Chem. Soc.*, 1914, xxxvi., 1916; *CHEMICAL NEWS*, 1914, cx., 224).

This work is a continuation of the preparation and investigation of the properties of the neutral ammonium salts of organic acids. This paper deals with the derivatives of benzoic acid. The salts described in the previous papers were prepared by passing dry ammonia into solutions of the organic acids in methyl alcohol, ethyl alcohol, ether, and acetone, or in mixtures of these solvents.

In the following work the neutral ammonium salts of *m*-toluic, *p*-toluic, *o*-chlorobenzoic, *m*-chlorobenzoic, *p*-chlorobenzoic, *o*-bromobenzoic, *m*-bromobenzoic, *p*-bromobenzoic, *o*-nitrobenzoic, *m*-nitrobenzoic, *p*-nitrobenzoic, 3,5-dinitrobenzoic, *o*-aminobenzoic, *m*-aminobenzoic, and *p*-aminobenzoic acids have been prepared by passing dry ammonia into solutions of the respective acids in the above anhydrous solvents, and some of their properties studied. After the salts were precipitated and tested for neutrality, they were filtered by suction on an alundum crucible and thoroughly washed with anhydrous ether. They were then put into crystallising dishes and allowed to stand a short time in a vacuum desiccator.

Several of the salts were also prepared in pure benzene. Currie (*Journ. Agr. Research*, 1914, ii., 8) states that the ammonium salts of weak organic acids can be prepared by passing dry ammonia into a benzene solution of the acids, and in this manner prepared the ammonium salts of caproic, caprylic, and capric acids.

The analysis of the salts consisted in determining the nitrogen by either the regular or a modified Kjeldahl method. In all the salts, except those of the three amino acids, the nitrogen present as "ammonium" nitrogen was determined. This is equal to the total nitrogen, except for the nitro acids. For the three amino acids, total nitrogen was determined. In the case of the *m*-nitro acid, both total and ammonium nitrogen were determined.

The Toluic Acids.

Ammonium *m*-Toluate.—No record can be found of the preparation and properties of this salt. It was prepared by passing dry ammonia gas into an ether solution of *m*-toluic acid. On passing in the gas, there was first formed an amorphous powder which, after a time, became crystalline. The powder, after being filtered, washed with ether, and dried, was dissolved in ethyl alcohol, from which it re-crystallised in the form of long prismatic needles. It crystallises from acetone in the same form. It is readily soluble in water, to which it imparts a neutral reaction. It is easily soluble in methyl alcohol, ethyl alcohol, and acetic acid. It is also soluble in acetone, but a little less so than in the last named solvents. The salt is somewhat hygroscopic, and gives off ammonia in the air. Determination of the nitrogen proved it to have the composition of the neutral salt.

Calculated for $C_8H_7O_2(NH_4)$, 9.15 per cent; found, 9.19 per cent N.

Ammonium *p*-Toluate.—Noad (*Ann.*, 1847, lxiii., 296) prepared this salt by neutralising an aqueous solution of the acid and allowing the solution to evaporate. The salt crystallised out in the form of small prisms. No analysis was made of the salt. Lossen (*Ann.*, 1897, ccxcviii., 72) found that the neutral salt could be prepared, in the form of clear flat cubes, by cautious evaporation of a solution of the acid in ammonia water. He also obtained it in glittering leafy crystals, upon the addition of an excess of alcoholic ammonia to an alcoholic solution of the acid. If an aqueous solution of this salt were boiled and the solution allowed to cool, needle-shaped crystals of the acid salt were obtained, which crystallised from alcohol in the form of large silvery white glistening leaves.

We prepared this salt by passing dry ammonia into an ether solution of *p*-toluic acid. It precipitated as a fine white crystalline powder, which formed small needles when re-crystallised from alcohol. The salt is soluble in water, methyl alcohol, ethyl alcohol, acetone, and acetic acid. It is insoluble in ether. The aqueous solution of the salt is at first neutral, but slowly becomes acid, due to hydrolysis. The salt is only slightly hygroscopic, and gives off ammonia slowly in moist air.

Calculated for $C_8H_7O_2(NH_4)$, 9.15 per cent; found, 9.06 and 9.11 per cent N.

The neutral ammonium salt of *o*-toluic acid has been previously prepared by one of us (McMaster, *Journ. Am. Chem. Soc.*, 1914, xxxvi., 1924). The neutral ammonium salts of the three toluic acids can thus be prepared in ether, but not in methyl or ethyl alcohols on account of their great solubility in these solvents. They form white crystalline precipitates, which are all soluble in water, acetone, and acetic acid. They are less soluble in acetone than in the other solvents. They are stable in dry air, and give off ammonia slowly in moist air. The *o*-toluate does not deliquesce, while the *m*- and *p*-salts do so very slightly. Their aqueous solutions are neutral.

The Chlorobenzoic Acids.

Ammonium *o*-Chlorobenzoate.—Rivals (*Ann. Chim. Phys.*, 1897, [7], xii., 521) mentions this salt as soluble in water with the absorption of a small amount of heat, but does not describe the method of preparation, the analysis, nor the properties of it. Korczynski (*Ann. Akad. Wissenschaften*, Krakau, 1908, 633; *Chem. Zentr.*, 1908, ii., 2009) states that solid *o*-chlorobenzoic acid combines with ammonia under pressure, forming $C_6H_4ClCOONH_4$, and that a second molecule of ammonia is taken up at -15° , which is quickly given off as the temperature rises to normal.

This salt can be prepared by the method described, in an ether solution of the acid, as a fine white powder. It is very soluble in water, methyl alcohol, ethyl alcohol, acetone, and acetic acid. It is only slightly soluble in ether. A solution of the salt in water is neutral, and does not hydrolyse even on long standing. The salt is not hygroscopic, and gives off ammonia only very slowly in both dry and moist air.

Calculated for $C_7H_4O_2Cl(NH_4)$, 8.07 per cent; found, 8.01 per cent N.

Ammonium *m*-Chlorobenzoate.—Gluud and Kempf (*Journ. Chem. Soc.*, 1913, ciii., 1533) have prepared this salt by heating the hydroxylamine salt of the acid to 170° , treating the mixture of the salt and the free acid obtained with warm xylene to remove the acid, extracting the ammonium salt with warm acetone, and then precipitating it with petroleum ether. It crystallises in small leaflets, which melted and decomposed at 203° to 204° after a short sintering. It dissolved in cold water, and in some organic solvents on heating, but so readily evolved ammonia that little but the free acid itself remained in solution. An aqueous solution of the salt also gave off ammonia on heating, and the acid crystallised out on cooling. They also prepared the salt by passing ammonia into a solution

of the acid in methyl alcohol and precipitating it with ether. They thus obtained glistening scales. No analysis was made of the salts obtained. Their first method of preparation could not have given a very pure product, since it depended on the selective solubility of the free acid and the salt, and since the solutions of the salt gave off ammonia on warming, even slightly so at ordinary temperatures.

This salt can easily be prepared by passing dry ammonia into an ether solution of *m*-chlorobenzoic acid. There is formed a fine white amorphous precipitate which, when crystallised from alcohol, gives a crystalline powder. It is readily soluble in water, methyl alcohol, and ethyl alcohol, and slowly so in acetic acid. It is insoluble in ether. The aqueous solution is at first neutral, but very slowly becomes acid. The salt does not give off ammonia in dry air, but is slightly deliquescent.

Calculated for $C_7H_4O_2Cl(NH_4)$, 8.07 per cent; found, 8.01 per cent N.

Ammonium *p*-Chlorobenzoate.—This salt was also prepared by Koryczynski (*loc. cit.*) by the same method used in the preparation of the *o*-compound. It can be prepared by passing ammonia into a saturated alcoholic solution of the acid. Glistening white laminae are thus formed. Upon passing ammonia into a solution of the acid in ether, a gelatinous precipitate is formed, which soon changes to a fine amorphous powder. This can be crystallised from acetone in the form of very fine needles. The salt is soluble in water, methyl and ethyl alcohols, and acetic acid. It is also somewhat soluble in acetone. The solution of the salt in water is at first neutral, but hydrolyses slowly on long standing. The salt does not deliquesce, and gives off ammonia only slowly in moist air.

Calculated for $C_7H_4O_2Cl(NH_4)$, 8.07 per cent; prepared in ether; found, 7.98 per cent N; prepared in ethyl alcohol; found, 8.04 per cent N.

The three chlorobenzoates can thus be readily prepared in ether. The *p*-salt can also be prepared in a saturated alcoholic solution of the acid. They are all soluble in water, methyl and ethyl alcohols, and acetic acid. They are also soluble in acetone, but to a less extent than in the alcohols and acetic acid. The *p*-salt is the least soluble of the three. The aqueous solutions of the *m*- and *p*-salts become slowly acid, but that of the *o*-salt is very stable. Only the *m*-salt is slightly hygroscopic, and all three give off ammonia very slowly in the air.

The Bromobenzoic Acids.

Ammonium *o*-Bromobenzoate.—No reference to this salt can be found in the literature. It can be prepared by passing dry ammonia into an ether solution of *o*-bromobenzoic acid. The salt at first precipitates as a slightly gelatinous mass, which soon changes to an amorphous powder. If ammonia is passed into an alcoholic solution of the acid, or into a solution of the acid in a mixture of equal volumes of ether and ethyl alcohol, no precipitate is formed; but if the latter solution is allowed to evaporate in the air the salt forms in crystalline tablets. The salt can also be prepared by passing ammonia into a solution of the acid in benzene, from which it precipitates slowly. A flocculent precipitate forms at first, and then changes to a fine powder. When re-crystallised from benzene it forms in fan-like groups of needles.

The salt is soluble in water, methyl and ethyl alcohols, and acetic acid. It is slightly soluble in acetone and insoluble in ether. The aqueous solution is neutral to sensitive litmus, there being no hydrolysis even on standing for several days. The salt is not deliquescent, is stable in dry air, and gives off ammonia very slowly in moist air. Analysis proved it to be the neutral anhydrous salt.

Calculated for $C_7H_4O_2Br(NH_4)$, 6.43 per cent; prepared in ether; found, 6.41 per cent N; prepared in benzene; found, 6.38 per cent N.

Ammonium *m*-Bromobenzoate.—As in the case of the *o*-bromobenzoate no reference to this salt can be found in the literature. It can be readily prepared in an alcohol-ether or in an ether solution of the acid. In the former it precipitates as silky crystalline flakes, and in the latter as a lustrous white semi-crystalline powder. It is very soluble in water, methyl alcohol, ethyl alcohol, and acetic acid. It is very slightly soluble in chloroform, and appreciably so in acetone, but insoluble in ether. The salt is not at all deliquescent. It gives off ammonia very slowly in dry air, and slightly more rapidly in moist air. The salt can also be precipitated in benzene as a milky white colloidal mass. Analysis was made of the salt prepared in ether.

Calculated for $C_7H_4O_2Br(NH_4)$, 6.43 per cent; found, 6.38 per cent N.

Ammonium *p*-Bromobenzoate.—This salt has been prepared by Koryczynski (*loc. cit.*) by the method described. It was prepared by us by passing ammonia into a solution of the acid in ether, in which it formed as a white amorphous compound. No precipitate was formed when the ammonia was passed into an alcoholic solution of the acid, but on evaporation aggregates of beautiful crystalline plates were formed. The salt is slightly soluble in cold water, but readily soluble in hot water. It is also soluble in methyl alcohol, ethyl alcohol, and acetic acid. It is slightly soluble in acetone and in chloroform. The solution in water is neutral at first, but hydrolyses slowly and becomes acid. The salt is not deliquescent, but gives off ammonia slowly in the air.

Analysis of the salt prepared in ether proved it to have the composition of the neutral salt.

Calculated for $C_7H_4O_2Br(NH_4)$, 6.43 per cent; found, 6.46 per cent N.

The neutral ammonium salts of the three bromobenzoic acids can thus be prepared in ether. The *o*-salt can also be prepared in benzene and the *m*-salt in an alcohol-ether mixture. They are soluble in water (the *p*-salt only appreciably so in hot water), methyl and ethyl alcohols, and acetic acid. They are slightly soluble in acetone and insoluble in ether. None of the salts are deliquescent.

The Nitrobenzoic Acids.

Ammonium *o*-Nitrobenzoate.—Koryczynski (*loc. cit.*) has also prepared this salt. It can also be prepared by conducting dry ammonia into a solution of the acid in anhydrous ether, or into a saturated solution of the acid in ethyl alcohol. It forms as a slightly yellowish white amorphous precipitate in ether, or as a white finely crystalline compound, having a decidedly yellowish tinge, in alcohol. It is soluble in water, methyl alcohol, ethyl alcohol, and acetic acid. It is moderately soluble in acetone. The salt is only slightly hygroscopic, and imparts a neutral reaction to a water solution of it. The aqueous solution slowly hydrolyses. The salt is fairly stable in the air, losing its ammonia but slowly in moist air.

Calculated for $C_7H_4NO_4(NH_4)$, 7.61 per cent; prepared in ether; found, 7.69 per cent ammonium N; prepared in ethyl alcohol; found, 7.59 per cent ammonium N.

Ammonium *m*-Nitrobenzoate.—Beilstein mentions the acid ammonium salt, $NH_4C_7H_4(NO_2)O_2 + C_7H_5(NO_2)O_2$. Koryczynski (*loc. cit.*) says that *m*-nitrobenzoic acid takes up one molecule of ammonia at room temperature and an additional molecule at 0° to -15° .

When ammonia is passed into a solution of *m*-nitrobenzoic acid in ether the neutral ammonium salt forms as a finely crystalline snow-white precipitate, soluble in water, methyl alcohol, ethyl alcohol, acetone, and acetic acid. It is insoluble in ether. Its solution in water is neutral. The salt is stable in both dry and moist air. Both the ammonium nitrogen and the total nitrogen in this salt were determined.

Calculated for $C_7H_4NO_4(NH_4)$, 7.61 per cent; found, 7.57 per cent ammonium N.

Calculated for $C_7H_3N_2O_4$, 15.22 per cent; found, 15.20 per cent total N.

Ammonium p-Nitrobenzoate.—Wilbrand and Beilstein (*Ann.*, 1863, cxxviii., 261) prepared this salt by dissolving the acid in concentrated ammonia water, and allowing the solution to evaporate to crystallisation. A hot solution of the salt produced, upon cooling, faint rose-red, much streaked, very glittering leaf-like crystals which were very easily decomposed. Korczynski (*loc. cit.*) also mentions this salt, but does not give its properties. We obtained this salt by our method in an ether solution as a snow-white amorphous powder, which on analysis proved to be the neutral salt. Some of the salt was re-crystallised from warm water in the form of small transparent leaflets. This was not analysed, but it was probably the acid salt, as the aqueous solution of the normal salt, which is neutral at first, quickly hydrolyses, and becomes acid, especially on warming. The colour mentioned by Wilbrand and Beilstein must have been due to impurities.

The neutral salt is soluble in water, slowly soluble in ethyl alcohol, readily soluble in methyl alcohol, and moderately soluble in acetone. It is insoluble in ether. It is not deliquescent, and does not lose ammonia in the air.

Calculated for $C_7H_4NO_4(NH_4)$, 7.61 per cent; found, 7.58 per cent ammonium N.

The three nitrobenzoates can thus be prepared in ether. They are soluble in water, in the common alcohols, and in acetic acid. They are less soluble in acetone than in the other solvents mentioned. Of the three, the β -salt is the least soluble in the organic solvents.

Ammonium 3,5-Dinitrobenzoate.—Mention is made of this salt by Korczynski (*loc. cit.*). Hubner (*Ann.*, 1883, ccxvii., 78) states that he used this salt in solution to prepare silver and copper *m*-dinitrobenzoates. He did not prepare the solid ammonium salt.

It can be prepared by passing ammonia into an ether solution of the acid as a white amorphous powder, having a slight yellowish tinge. It is soluble in water, methyl alcohol, ethyl alcohol, acetic acid, benzene, and carbon tetrachloride. It is somewhat soluble in acetone, but less so than in the other solvents mentioned. It is insoluble in ether. The salt is not deliquescent. It is stable in dry air, but loses its ammonia very slowly in moist air. Its aqueous solution is neutral, and does not hydrolyse even on standing for several days.

Calculated for $C_7H_3N_2O_6(NH_4)$, 6.12 per cent; found, 6.11 per cent ammonium N.

The Aminobenzoic Acids.

Ammonium o-Aminobenzoate.—This salt can be prepared either in ether or in a mixture of one volume of acetone and two volumes of ether. When prepared in ether it is a white amorphous powder, while in the acetone-ether mixture it forms fine white needles. It is very soluble in water, the solution being neutral at first but soon becoming acid. The salt is also very soluble in methyl and ethyl alcohols and acetic acid. It is moderately soluble in acetone and only slightly so in ether. It is slightly deliquescent. It does not lose ammonia in dry air and only slowly in moist air.

Calculated for $C_7H_{10}N_2O_2$, 18.18 per cent; found 18.14 per cent total N.

This analysis was made on the salt prepared in ether, and proved that we had obtained the neutral ammonium salt. Although some of the salts of *o*-aminobenzoic acid have been prepared and studied, no mention of the neutral ammonium salt can be found.

Ammonium m-Aminobenzoate.—As in the case of the ammonium *o*-aminobenzoate no reference to this salt can be found in the literature. It can be prepared by pouring

a saturated solution of the acid into absolute ethyl alcohol, into which dry ammonia has been passed for some time, into a large amount of ether. Although the salt is only slightly soluble in ether it cannot be prepared directly in ether since the free acid is also only slightly soluble in that solvent. While filtering off the salt, prepared as above described, it is necessary to keep the alundum crucible filled with ether to prevent the salt going into solution on account of the alcohol present. The salt dried in a vacuum desiccator to a white, yellow-tinged, flaky crystalline compound. The salt cannot be prepared by passing dry ammonia into a solution of the acid in methyl alcohol, ethyl alcohol, propyl alcohol, acetone, benzene, toluene, pyridine, carbon tetrachloride, or carbon disulphide on account of its great solubility in these solvents. It is also soluble in acetic acid and ethyl acetate. It is only slightly deliquescent. It does not lose ammonia in dry air, but gives it off slowly in moist air.

Calculated for $C_7H_{10}N_2O_2$, 18.18 per cent; found, 18.12 per cent total N.

Ammonium p-Aminobenzoate.—Likewise no mention of this salt can be found. When ammonia is passed into an ether solution of the acid the salt forms as a white amorphous precipitate. It is soluble in water, methyl alcohol, ethyl alcohol, acetic acid, and acetone. It is only slightly soluble in ether. The salt is not deliquescent, and its aqueous solution is neutral to sensitive litmus-paper. It is stable in dry air and slowly loses its ammonia in moist air.

Calculated for $C_7H_{10}N_2O_2$, 18.18 per cent; found 18.17 per cent total N.

The ammonium salts of the three aminobenzoic acids can be prepared in an ether solution by the general method described, modifying the method in the case of the *m*-salt by pouring the saturated alcoholic solution into an excess of ether. The three salts are soluble in water, the alcohols, acetone, and acetic acid.

Ammonium 3,5-Diaminobenzoate.—After having so easily prepared the ammonium salts of the nitrobenzoic acids, the 3,5 dinitrobenzoic acid, and the aminobenzoic acids, an attempt was made to prepare the ammonium salt of 3,5-diaminobenzoic acid by passing dry ammonia into a solution of the acid in different organic solvents. Saturated solutions of the acid in methyl alcohol, ethyl alcohol, ether, benzene, and carbon tetrachloride were tried, but no precipitate formed owing evidently to the extreme solubility of the salt in these solvents. Further attempts will be made to prepare this salt and study its properties.

This investigation is being continued with other organic acids, especially the substituted acids.—*Journal of the American Chemical Society*, xxxvii., No. 9.

AN INVESTIGATION OF THE EXTRACTION OF POTASH FROM FELSPAR.

By ELWIN H. QUINNEY.

THE vast amount of potash locked up in felspars and feldspathic rocks, and the great demand which has recently arisen for an American supply of potash in available form for agriculture, has stimulated not only a search for new deposits, but has caused many of the best chemists of our country to search for a method by which this potash can be made available on a commercial scale. The natural silicates commercially available as sources of potash are chiefly orthoclase and leucite. Both of these minerals are potassium aluminum silicates. The theoretical formula for orthoclase is $K_2O \cdot Al_2O_3 \cdot 6SiO_2$, and for leucite $K_2O \cdot Al_2O_3 \cdot 4SiO_2$. The principal sodium felspar, albite, has the theoretical formula $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$. It is well known that these felspars run into and substitute each other in various proportions, so that different pro-

ducts will vary widely in respect to their soda, potash, and aluminum contents. Iron is often found associated with these minerals.

The following investigation was carried on at the South Dakota State School of Mines, with the supervision and assistance of Prof. M. F. Coolbaugh. The rock used was a crystalline orthoclase felspar, which contained 9.02 per cent K_2O , 21.30 per cent Al_2O_3 , 1.60 per cent Fe_2O_3 , and 62.10 per cent SiO_2 .

The Gypsum Method.

The sample of felspar was heated with an excess of gypsum. After leaching with water an appreciable amount of potassium was found in the filtrate, and the quantitative investigation was begun.

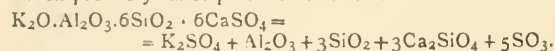
A series of experiments with felspar and gypsum heated to a high temperature gave the results shown in Table I.

TABLE I.—Gypsum Method.

No.	Proportion.		Number of full power Bunsen flames.	Time of heating. Hours.	K_2O extracted. Per cent.	Extraction. Per cent.
	Parts of felspar.	Parts of gypsum.				
1.	2	1	1	2	1.36	15.00
2.	1	1	1	1	1.72	19.00
3.	1	2	2	1	2.47	27.40
4.	1	8	2	2	8.84	98.00

Although a very satisfactory extraction by this method was obtained, it can readily be seen that it could never be made a commercial success because of the great decrease in per cent of potash in the final product.

The law of mass action explains this large amount of gypsum necessary to get the extraction. The reaction which probably takes place is as follows:—



The theoretical amount of $CaSO_4$ required to complete the reaction is 0.735 grm., when 0.5 grm. of felspar is taken, or about one part felspar to one and one-half parts $CaSO_4$. But, as shown above (Table I.), the reaction is evidently not completed with two parts of $CaSO_4$. However, when the mass of $CaSO_4$ is increased to eight parts, the reaction is nearly completed.

Salt and Sulphuric Acid Method.

The problem then seemed to be to find something that would unite more quickly with the felspar and not be influenced by the law of mass action.

TABLE II.—Salt and Sulphuric Acid Method.

No.	Charge.			Time and Method of heating.	K_2O Per cent.	Extraction. P. cent.
	Felspar. Grm.	$NaCl$. Grm.	H_2SO_4 . Grm.			
1.	0.5	0.12	Excess	60 Hot plate	1.25	13.85
2.	0.5	0.15	"	20 Dull redness	0.32	3.55
3.	0.5	0.15	"	30 1 Flame	0.78	8.86
4.	0.5	0.15	"	45 2 Flame	4.32	47.89
5.	0.5	0.15	"	45 Dull redness	1.66	18.40
6.	0.5	0.25	"	40 1 Flame	3.12	34.59
7.	0.5	0.25	"	60 2 Flame	3.79	42.01
8.	0.5	0.25	"	60 Dull redness	1.57	17.40
9.	0.5	0.50	"	60 2 Flame	5.56	61.64
10.*	0.5	0.25	"	20 Blast	2.96	32.81
11.*	0.5	0.36	"	10 "	4.05	44.67
12.*	0.5	0.36	"	10 "	4.36	48.34
13.*	0.5	0.36	"	20 "	5.32	59.00
14.†	0.5	0.36	"	20 "	5.76	63.85
15.*	0.5	0.36	"	20 "	5.32	59.00
16.†	0.5	0.31	"	15 "	4.87	54.00
17.‡	0.5	0.60	"	20 "	7.60	84.62
18.§	0.5	0.41	"	20 "	5.08	56.32
19.‡	0.5	0.41	"	20 "	4.50	49.88

* Heated for one hour before blasting.

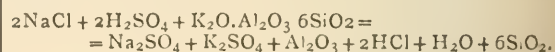
† Heated for 45 minutes before blasting.

‡ Heated for 1½ hours before blasting.

§ Heated for 1 hour and ten minutes before blasting.

Since chlorine unites very readily with potassium it was reasoned that if this element could be liberated in a mixture it might solve the problem. Naturally the cheapest possible materials were selected from which to make the chlorine, namely, salt and sulphuric acid. The method employed was to heat the felspar with a certain quantity of salt and sulphuric acid. A large number of tests were run according to this method before anything like uniform results were obtained. Table II. is a tabulation of the results.

As shown above, a few tests were made at very low temperatures. At first these looked promising, for a decided reaction of some sort had taken place, the whole mass turning to a white cake. When the temperature was increased a little, as in No. 3, the iron seemed all to go to the oxide, giving the mass a reddish tinge when cold. The extraction, however, was very low, and proved that the change was due to the salt and sulphuric acid alone and not to any reaction with the felspar. By keeping the amount of salt constant and varying the temperature and *vice versa* it was discovered that both the amount of salt and the temperature affected the reaction. The probable reaction is as follows:—



Assuming that the reaction of the potassium and chlorine would go to completion before the aluminum was attacked, and since the amount of chlorine necessary is directly proportional to the salt, it was figured that the amount of salt necessary to unite with the potassium would be about one part to two parts felspar. This proportion, even with the highest temperature, gave less than 50 per cent extraction. By increasing the mass of salt somewhat a trifle better results were obtained, but still too low. The amount of salt necessary to unite with both the potassium and aluminum was then added. This was found to be about four parts salt to five parts felspar. By increasing the mass of salt from this to about six parts to about five parts felspar a fair extraction was obtained. The foregoing experiments disclosed the facts that the extraction was proportional to the amount of salt added and also to the temperature at which the mixture was heated. The next step was a series of tests made by heating in an assay muffle, so that the temperature be more uniformly controlled. The results obtained are shown in Table III.

TABLE III.—Salt and Sulphuric Acid Method heated in Assay Muffle.

No.	Charges.			Time of heating. Hours.	Approximate temperature. °C.	K_2O Percent.	Extraction. P. c.
	Rock. Grm.	$NaCl$. Grm.	H_2SO_4 . Drops.				
1.*	0.5	0.31	4	1	1000	4.25	47.12
2.*	0.5	0.40	4	1	1000	5.08	56.32
3.*	0.5	0.50	4	1	1000	4.36	51.36
4.†	0.5	0.31	4	2	1200	5.14	57.00
5.†	0.5	0.40	4	2	1200	6.63	73.50
6.†	0.5	0.50	4	2	1200	7.42	82.26

* Did not fuse.

† Black, glassy fusion.

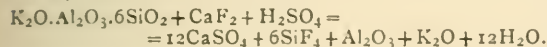
‡ Green, glassy fusion.

The law of mass action evidently enters into this reaction also, and by increasing the mass of salt a complete extraction could be obtained, but by so doing would again make the process worthless from a commercial standpoint by decreasing the percentage of potassium in the final product. For example, take the best extraction obtained, 84 per cent, or 7.60 per cent of the potash. This would give only 5.06 per cent potash in the final product, which is as low as could be worked profitably. There is one great advantage in this process which may make it valuable: it could be used in connection with the manufacture of hydrochloric acid. The felspar could be added

to the salt and sulphuric acid, and a by-product containing soluble potash would be left in the residue, with no loss of hydrochloric acid.

Calcium Fluoride Method.

Since hydrofluoric acid is the best solvent for silica, it was reasoned that it might be used to dissolve this constituent and leave the potassium and aluminum free to unite with a mineral acid. Calcium fluoride (CaF_2), being the most available compound of fluorine, it was used with sulphuric acid to form the hydrofluoric acid, according to the following reaction:— $\text{CaF}_2 + \text{H}_2\text{SO}_4 = \text{CaSO}_4 + 2\text{HF}$, or with felspar—



The amount of calcium fluoride necessary to complete the reaction is 0.84 gm. to 0.5 gm. felspar. Only one test was run using these proportions and only 37 per cent extraction was obtained. It is out of the question to increase the mass here.

Phosphate Rock Method.

One more method was tried to a very limited extent. From previous experiments (gypsum method) it will be noted that dicalcium silicate was formed. If the calcium from the ordinary phosphate rock could be used to unite with the silicate of felspar, we would then have a final product containing both potash and phosphorus, which would make it doubly valuable as a fertiliser. With this in view the amount of phosphate rock necessary to unite with the silica of the felspar was figured to be about 1.12 grms. when 0.5 gm. of felspar was taken. Sulphuric acid being also added in slight excess. This mixture was heated as in previous experiments and extracted with dilute sulphuric acid. Two tests were made by this method, both giving low results, one 21 per cent and the other 22 per cent extraction.

The foregoing experiments cover well the investigation of the principles of many of the old methods as well as the new ones here worked out, and while ideal results were not obtained many new and interesting facts were brought to light. All work was done with extreme care and developments watched very closely. No results are tabulated here that were at all doubtful.

The above paper is a thesis presented by Mr. Quinney to the faculty of the State School of Mines for the degree of Metallurgical Engineer. It is of interest to note that subsequent to the presentation of the thesis Mr. Quinney and Prof. M. F. Coolbaugh did a considerable amount of investigation with the idea of developing if possible a process for the production of potassium and aluminum in a commercial way. This subsequent work resulted satisfactorily, and in connection with Attorneys C. L. Lewis and J. F. Schrader, of Rapid City, they secured a patent. A brief description of this patent is given in the *Official Gazette* of the United States Patent Office, ccx., No. 2. Tuesday, January 12, 1915. The patent is No. 1,125,007, and is entitled "Process of Producing Soluble Salts of Potassium and Aluminum." A description is given in the above-named publication as follows:—

"1. The herein described process of producing soluble salts of aluminum and potassium from siliceous rocks, earths, or minerals, containing insoluble compounds of potassium and aluminum, which consists in reducing the rocks, earths, or minerals to a powdered form, mixing therewith limestone in the approximate proportions of one and seven-tenths parts of limestone by weight to each one part of silica by weight contained in said rocks, earths, or minerals, heating the mixture to incipient fusion, cooling quickly, leaching the product with dilute sulphuric acid in the approximate proportions of one and two-tenths parts of sulphuric acid by weight to each one part of potash by weight, and three parts of sulphuric acid by weight to each one part of alumina by weight, and subsequently separating the potassium and aluminum sulphates from the resulting solutions.

"2. The herein described process of producing soluble salts of aluminum and potassium from siliceous rocks, earths, or minerals containing insoluble compounds of potassium and aluminum, which consists in reducing the rocks, earths, or minerals to powdered form, mixing therewith limestone in the approximate proportions of one and seven-tenths parts of limestone by weight to each one part of silica by weight contained in said rocks, earths, or minerals, heating the mixture to incipient fusion, cooling quickly, leaching the product with dilute sulphuric acid, and separating the potassium and aluminum sulphates from the resulting solutions by crystallisation.

"3. The herein described process of producing soluble salts of aluminum and potassium from siliceous rocks, earths, or minerals containing insoluble compounds of potassium and aluminum, which consists in reducing the rocks, earths, or minerals to a powdered form, mixing therewith limestone in the approximate proportions of one and seven-tenths parts of limestone by weight to each one part of silica by weight contained in said rocks, earths, or minerals, heating the mixture to incipient fusion, cooling quickly, leaching the product with dilute sulphuric acid in the approximate proportions of one and two-tenths parts of sulphuric acid by weight to each one part of potash by weight, and three parts of sulphuric acid by weight to each one part of alumina by weight, and subsequently separating the potassium and aluminum sulphates from the resulting solutions by crystallisation."—*Chemical Engineer*, xxi., No. 4.

THE DETERMINATION OF CHROMIUM AND MANGANESE IN IRON AND STEEL.

By FRED C. T. DANIELS.

In steel furnace operations it is frequently necessary to include chromium among elements to be determined in the preliminary analysis. The following 20-minute method has been worked out to fill this necessity. It has been in constant use for the past two years, and is sufficiently accurate to be used as a daily routine method, and it occupies but little of the chemist's actual working time.

The method for chromium is an adaptation of the persulphate method for the manganese determination in iron and steel.

The method for manganese is the persulphate method, except that the sum of the manganese and chromium is obtained in this titration and the manganese calculated by difference, using the results from the chromium determination. The objection to the usual persulphate method for manganese in the presence of chromium is that a varying quantity of the chromium is reduced along with the manganese by the ferrous ammonium sulphate or sodium arsenite. If determined colorimetrically the chromium gives the solution a different shade, which is difficult to compare. This may be overcome by using for a standard a steel containing approximately the same amount of chromium as the sample. A still more convenient way is to add the chromium as potassium bichromate, using a standard solution, so that 1 cc. would equal 0.0005 gm. of chromium, i.e., 0.25 per cent chromium for a 0.20 gm. charge of the sample. This solution is added to the standard after the solutions have been transferred to the colour comparison tubes.

Chromium.—Weigh 1 gm. of the sample into a 300 cc. Erlenmeyer flask (Jena glass), add 100 cc. nitric acid (1.135 sp. gr.), place on the hot plate, and when solution is complete boil off all nitrous fumes. (The volume of the solution should not be less than 75 cc. It is unnecessary to filter off the silicon and graphite residue if the solution is complete. When the sample is high in combined carbon it is well to add a few crystals of ammonium persulphate when the solution is complete, and boil a moment longer to destroy the combined carbon).

Remove the flask from the hot plate, add 75 cc. silver nitrate solution (2 grms. per litre), and immediately 5 grms. of ammonium persulphate crystals. Replace flask on the hot plate and bring gently to boiling. Boil vigorously for a minute, and while still boiling add dilute hydrochloric acid drop by drop until the permanganate colour is completely destroyed. Continue the boiling for one minute, and then cool the flask immediately in water. Titrate by adding an excess of tenth-normal ferrous ammonium sulphate solution above that required to reduce the chromium, and titrate back with tenth-normal potassium permanganate solution. The number of cubic centimetres of the ferrous ammonium sulphate oxidised by the chromate, multiplied by 0.00174, gives the weight of chromium in the sample.

Manganese in the Presence of Chromium.—Proceed according to the above directions for the determination of chromium except that after the ammonium persulphate is added only heat until the solution just comes to boiling, then cool immediately and titrate as before, this time adding enough ferrous ammonium sulphate to reduce both the manganese and chromium. The number of cubic centimetres of ferrous ammonium sulphate used, minus the number used in the chromium determination multiplied by 0.0055, equals the weight of manganese in the sample.

The ultimate value of the solutions may be used in calculations as above. In this case it is advisable to carry along a blank with a sample containing no chromium and subtracting the blank. The standardisation of the solutions against a standard steel is the most satisfactory procedure.—*Chemical Engineer*, xxi., No. 6.

SOME PROBLEMS OF CHEMICAL INDUSTRY.*

By RAYMOND F. BACON,
Director of the Mellon Institute of Industrial Research and School
of Specific Industries of the University of Pittsburgh.

THE industrial researcher who deals with the processes of manufacture and the phenomena of reactions involved is becoming less and less regarded as a burden unwarranted by returns. The aim of every industrial operation is toward perfection, both in process and the necessary mechanical equipment, and every new development in manufacturing creates new problems. It follows, then, that the greater the number of researches the greater is the progress in a given field and the greater becomes the number of new problems. Moreover one can only conclude that, since perfection is but, after all, an ideal, no industrial field has been sufficiently investigated.

The thirst for distinction and wealth kindles the lamp of invention, and the light of the knowledge resulting from discoveries and improvements in manufacturing operations has so emboldened us that some industries now consider themselves capable of solving any problem. This has been shown in innumerable instances, but is particularly true of the great chemical industry, which, while its achievements have been stupendous, is nevertheless confronted with many problems of importance. With your permission I shall restrict myself to recounting some of the problems which engage the attention of the present-day chemical industrialist, problems which he is capable of clearing up provided the service of research is called to his aid, but which have so far remained unsolved. In collating these I have drawn from all available sources of information and from my own experience.

Some Metallurgical Problems of To-day.

While there may not be at the present time room for such abnormal discoveries in siderurgy as in the past, investigators are quietly and steadily augmenting our

knowledge of iron and its alloys, and the value of such research work is generally recognised. Elaborate investigations are constantly being conducted by several manufacturers, especially by the United States Steel Corporation, which has to date expended over 800,000 dol. in studies on the electrothermic production of steel alone. However, metallurgical research laboratories are still comparatively uncommon. Very few iron furnaces or smelting plants are without a control laboratory, which has come about notwithstanding the opposition of "practical men," and the research laboratory will eventually win a similar victory. Such problems as the working up of blast-furnace slags by an economic process could probably be solved by systematic research.

The great problems at present in the metallurgy of zinc are in concentration of the ore and in the treatment of flotation concentrate. The latter produces the troubles that fine ore always does: it is difficult to roast, and the distillation of it is attended with troubles. Viewing the present status of the practice in zinc smelting one is impressed by the high extraction results, the low fuel consumption made possible by regenerative gas-firing, and the reduction of labour involved in the art.

In copper metallurgy, the leaching of copper ores and electrolytic deposition for precipitating are receiving increased attention. With regard to chemical precipitation it is desirable that this process be conducted in such a way as to regenerate the solution. In electrolytic copper refining promising progress has been made in the treatment of anode slimes, and increasing attention is being paid to the recovery of by-products. Then, too, the progress in the development of flotation processes has been phenomenal, but still our knowledge regarding flotation is meagre.

The search for platinum substitutes continues, and an economic method for rapidly separating the metals of the platinum group is also desired.

The brass industry has been carried on for more than a century in Connecticut, and considerable study has been given the matter of zinc loss, but so far those engaged in the industry have been unable to find any economic and entirely satisfactory method to overcome such loss. Moreover, no entirely satisfactory gas furnace has been designed for general brass rolling mill practice.

The development in engineering construction has arrived at a point where the use of special alloys for specific requirements requires more thorough investigation. The matter of corrosion has been one of a more or less mysterious nature; confusion has arisen on account of the names of alloys; the ideal alloy for condenser tubes has not been found; the failures of screens made from brass wire are well known, and we have yet to find an aluminium alloy that will resist alkalis. It is true that there is beginning to be a well-defined literature on the subject of alloys, and that now one can sometimes very closely predict the properties of combinations of the more commonly known metals, but we have not begun to open up the possibilities of usefulness in the exploration of the alloy field, in which I include the so-called "dilute alloys"—cases wherein a very small amount of a metal alloyed with, say, iron or steel confers upon it some new or unusual properties.

Some Problems of Industrial Inorganic Chemistry.

Nitrous oxide is being successfully used in combination with oxygen for the production of anaesthesia, but while there is a material available for the production of oxygen upon treatment with water ("oxone") no substance which will yield nitrous oxide upon similar treatment is known. On account of the present large consumption of nitrous oxide considerable study has been devoted to this problem.

New uses, one such as would increase the demand, for the following products are required:—Potassium hydroxide, chlorine, bleaching powder, bromine and bromides, calcium, silicon, selenium, tellurium, cobalt,

* Author's abstract of an Address delivered before the Chicago Section of the American Chemical Society on May 14, 1915.

uranium, and molybdenum. Since sodium metantimonate is undesirable in enamels placed on cooking utensils, new uses for this and other antimony compounds are needed; attention may be directed to the fact that antimony lithopones, made by treating barium carbonate and antimony sulphite, offer perhaps a partial solution of this problem. It may be noted here that a large production of arsenic would follow a demand.

In the domain of ceramics the subject of binders presents a field for research; to cite a simple instance, a binder for infusorial earth that is cheap and will stand a temperature of about 3000° F. is being sought for by those interested in the production of metallurgical brick.

Efforts to improve the quality of all varieties of clay goods, from ordinary brick to the highest-grade pottery, are constantly in progress by American clay-workers; this is evinced by the new shades and texture of building brick, the new forms of hollow building tile or block, and the new effects in terra cotta that are being put on the market, and by a general improvement in the higher grades of pottery. Of interest in this connection is the realisation of the value of American clays in glass-pot manufacture. Earthenware kilns, designed in such a manner as to reduce the carrying of heavy weights, to do away with working in hot kilns, and to diminish the handling of dipped ware, would be very desirable, and some progress in tunnel kilns of this general type has been made in England.

It has been said that the technology of common earthenware, Rockingham ware, majolica, faience, and stoneware is comparatively simple. This is undoubtedly correct, viewing the pottery industry as it exists to-day, but it is also true that less advantage has been taken of scientific research in earthenware manufacture than in many other industries. A familiar problem is the nature of clay plasticity, which is quite open for study; the flowage behaviour under pressure promises to be of value in this work.

There are many problems to be found in the glass industry; for example, the available results relating to the problem of strains in glass merely represent a beginning of the work necessary to a complete solution. However, the troubles of the glass manufacturer would vanish if the chemical constitution of glass were definitely determined, and if the ideal non-contaminating container (pot and tank) were found. A great problem in the glass industry is the better utilisation of heat; only 5 per cent is actually utilised in making glass.

In the tinning industry electro tinning has recently made important progress, although as yet no marked commercial success has been attained, and a beginning has been made toward coating black plates with aluminium by a cold, wet electric process. Among the problems worthy of investigation in connection with the tinplate industry are the following:—

1. Over and under black pickling, the influence of strength and temperature of the acid solution, and of time. Mention may be made here that the utilisation of spent ferrous liquor obtained in pickling iron or steel is receiving more and more attention. (Note 1). Perhaps the acid and a paint pigment could be recovered from waste hydrochloric acid pickle liquor by a simple heat treatment in a suitable apparatus.

2. Effect of varying temperatures and time of annealing.

3. Light and heavy cold rolling.

4. Temperature effects in the tinning operations.

5. Differences from the tinplate trade point of view between acid Bessemer steel, basic Bessemer steel, acid open-hearth steel, and basic open-hearth steel, and the comparative tin consumption of each kind.

Since the mantle industry cannot absorb more thorium (about 300 tons of thorium nitrate are consumed annually), and much larger quantities of mesothorium than 6 grms. (present available supply under normal conditions from 3300 tons of monazite sand) will probably be re-

quired for therapeutic purposes, the extraction of larger quantities of mesothorium depends upon profitable utilisation of cerium (over 1000 tons of ceria are obtained annually in the mantle industry and only three tons are required in the manufacture of mantles). Of 1000 tons of ceria, 200 tons are normally used in the manufacture of pyrophoric alloys, 300 tons are used in the form of fluoride for impregnating arc-light carbons, and the dyeing and photographic industries take small amounts. New uses are consequently wanted for cerium compounds, which might be used, for instance, in the weighting of silk.

Chemistry is a very important factor indeed in the fertiliser industry, and it will of course carry out the work ahead. Some of the problems are:—

1. Rendering available the phosphoric acid in refractory minerals by, say, electrochemical means of a suitable nature.

2. Recovery by economical processes of potash from feldspar, alunite, leucite, and beet-sugar molasses. In the case of the production from minerals the cost of treating feldspars has so far been prohibitive; electrothermic processes will undoubtedly be eventually used. It may also be possible to recover thus the potash contained in the raw materials used in the cement industry, and some progress has in fact been made in the solution of this problem. My own opinion is that the successful potash recovery process will be one in which the principal product will be one other than potash, and the latter will be a by-product.

Some Problems of Industrial Organic Chemistry.

In the wood distillation industry new uses, immune from the competition of denatured alcohol, are anxiously desired for methyl alcohol. A more rational utilisation of wood-tar is also essential for the future of this industry; this is no reason why valuable by-products other than creosote and shingle stains might not be obtained from hardwood-tar. In this connection an economic—direct, if possible—process for manufacturing acetaldehyde (for use as an acetylene solvent) from acetate of lime would undoubtedly attract the producers of the latter, as would also important new uses for acetone. It is rather surprising that the manufacture of acetic acid from acetate of lime has been neglected in the United States. Hardwoods abound on the Pacific coast and can be distilled with profit, providing markets for the charcoal and calcium acetate can be created.

Commercially operable processes for the manufacture of charcoal, cellulose, gas, glucose, or ethyl alcohol from wood waste are occasionally inquired for. A number of methods have been devised, but economies must be developed.

It may be mentioned in this place that pinene has been shown to be the chief source of isoprene in turpentine. A process for economically increasing the yield of pinene in the distillation of long-leaf pine would possess commercial value, both from a synthetic rubber and from a turpentine standpoint.

There are many chemical problems in paper-making. What, for instance, is the influence of chemicals on the "beating" process? The bleaching problem has also been very little studied; it is unknown, for example, what is the exact nature of the substances removed from the pulp by bleaching, or in what form they are eliminated. Then, too, the problem of sizing is full of unsolved points; the fixation of the loading materials is a physico-chemical problem which should repay systematic investigation, and the question of new sizing agents awaits solution. Other of the many problems are the following:—What are the chemical causes of the loss of resistance to ink after storage, particularly in the case of engine-sized paper? What are the chemical relations of the dyestuff towards the mineral loading materials in pulp-dyeing? (Note 2). And then there is the problem of the clarification of the machine waste waters and the recovery of by-products therefrom. In spite of the fact that a tremendous amount

of work has been done on the problem of the waste liquor from sulphite pulp mills, it still remains for the most part unsolved.

On account of the war, now would be a most opportune time to lay the foundation for an artificial silk industry in this country.

The manufacturers of the chlorides of carbon would be interested in new commercial uses for carbon tetrachloride, dichloromethane, and hexachlorethane. An economic commercial process for chlorinating natural gas rich in methane would be attractive; a number of such processes have been worked out, but apparently these leave something to be desired.

Among other problems awaiting technical solution are:—The production of oxalic acid by the electrolytic oxidation of cellulose; the production of acetaldehyde and acetic acid from acetylene; the device of ways and means to use the lower grades of gasoline in internal combustion motors; an economic process for removing resin from fir and other wood in pulp-making; the production of permanent light shades on glove leather; more efficient processes for depilating, disinfecting, deliming, softening, and waterproofing skins and hides, and for brightening tanned skins, and the utilisation of the fibrous wastes in several industries, especially the million bushels of envelopes decorticated from buckwheat annually. Novel processes for the refining or bleaching of vegetable oils, especially of cottonseed and soy-bean oils, always interest the refiners of these. And finally it may be mentioned here that the wine-growers of California and New York now have the opportunity to produce argol, and thus begin the manufacture of tartaric acid.

As instances of some desirable commercial syntheses, mention may be made of the fact that processes are wanted for the synthesis of acetylene, formaldehyde, amyl alcohol, tartaric and citric acids, sanguinarine, hydrastine, and nicotine.

In the explosives industry the manufacturers of nitroglycerin hope that in synthetic glycol may be found the solution of their bondage to the fluctuation of the corn and cottonseed crops. The production of glycerin depends considerably on the abundance or otherwise of pork and of cottonseed oil, and the former depends largely on the corn supply.

In depolymerising heavy hydrocarbon oils, hydrogenation with platinum black could be accomplished if an antidote could be found for the poisonous effect of sulphur compounds. Oil refiners are endeavouring to find methods to convert every pound of gas oil into more valuable products, especially motor fuel. (Note 3). Through the application of physicochemical principles to the "cracking" of oil, a better control of and greater flexibility in the resultant end-products can be expected. This means that if gas manufacturers are to continue the use of petroleum in carburetting water-gas, they must resort to one of two alternatives:—

1. Greatly increase the yield of gaseous hydrocarbons from a given amount of oil; or

2. Perfect methods of using the millions of barrels of fuel oil which are at present considered unfit for carburetting water-gas.

Much also remains to be done in the field of concentration, pressure, and contact-surface changes with respect to illuminating and heating gas.

Sugar manufacturers do not work up their by-products; for example, they do not can molasses or manufacture alcohol from it. Molasses is a suitable source of alcohol; the by-products are yeast, fusel oil, and carbon dioxide. There is little co-operation among sugar manufacturers to improve methods. No limits have been scientifically set for moisture content and degree of infection of sugar, the two greatest points in grading sugars for storage, and the cause and prevention of infection require study along broad lines. Then, too, much remains to be learned concerning bone-black. A satisfactory drying process must be found to render the mud from sugar refineries

available for use as a fertiliser, and sugar-beet wastes could furnish about 15,000 tons of potash annually.

In the rubber industry there are four leading groups of problems—quality of natural raw rubber, synthetic rubber, vulcanisation, and regeneration. The viscosity of Hevea latex diminishes upon dilution with water in such a manner as to suggest that it is an emulsion rather than a suspension. Since, however, rubber is an emulsoid colloid, and consequently always a liquid, we are not able in this way to draw any conclusion as to the state of polymerisation in the latex. The nature of coagulation has not been fully explained, although it is of absolutely vital importance as regards the quality of the rubber produced. No chemical explanation can at present be given to account for the differences in quality between Para and plantation rubber. Research is also required to determine the nature of the factors affecting the quality of raw rubber and its velocity of vulcanisation. It is important to have a raw rubber which shall vulcanise at a constant speed, and if possible of guaranteeing this by careful tests before buying. Rubber from which the resins or proteins have been removed will not vulcanise as readily as ordinary technically pure rubber, and the conclusion has been drawn that synthetic rubber will be bad on the ground of its being too pure. The rubber manufacturer will not, however, be in any way embarrassed on that account, and will be able to add as much resin as is needed, consistent of course with specific work. With regard to the regeneration of waste vulcanised rubber, so far it has not proved possible to obtain from waste vulcanised rubber a product like new rubber and containing no sulphur. The combined sulphur is bound with extraordinary strength. What can be accomplished is to remove the free sulphur, some or all of the mineral fillers, and the fibrous materials, and the reclaimed rubber thus obtained by many processes is a valuable adjunct in cheap mixings.

Certain problems connected with the coal-tar industry are as follows:—

1. The devising of a practical distillation method for increasing the yield of coal-tar light oil (at present the yield is never over 4 per cent and averages about 2 per cent).

2. New uses for hard-coal tar pitch—ones other than as a briquette binder. This investigation would have for its object the extension of the demand for this constituent of tar.

3. A commercially successful, economic method of dehydrating tar. While the water may be reduced to less than 0.5 per cent by heating the tar continuously in thin films under a partial vacuum (this plan is most in favour), it is said that any improvement in this troublesome and expensive step would be welcome.

4. An investigation to find special fields for the use of water-gas tar and its products, especially the pitch (which shows to a much higher degree than coal-tar pitch the properties of brittleness and susceptibility to temperature changes) and oils (which have not given the great value for timber preservation characteristic of the coal-tar oils).

5. New uses for anthracene (other than as a basis for alizarin, &c.) in this country. The object would be the finding of such uses as would make the production of anthracene profitable.

6. The chlorination of naphthalene. The wax products obtainable thereby possess dielectric properties, and promise to develop an important field. An investigation of the methods of preparing these, their properties and commercial values, along broad lines would undoubtedly lead to important technical results.

Owing to the great number of existing technochemical problems I have restricted myself in the choice of the ones cited, and in general have refrained from even a cursory discussion thereof. I have endeavoured, however, within the brief period of thirty minutes to show that many various problems await solution, and that a number of branches of chemical industry invite research.

It was for the purpose of aiding manufacturers in solving

just such problems as have been mentioned that the Mellon Institute of Industrial Research was founded. I now invite you to make a visit of inspection to the new home of this representation of an alliance between industry and learning which has been gratifyingly successful, in order that you may see what we are accomplishing in obviating difficulties in manufacture, in utilising wastes, in improving and cheapening manufactured products, in finding new uses for products, and in searching for new and useful products for twenty five American industrialists.

Notes.

1. Of a similar nature is the problem of the economic utilisation of mine water, which resolves itself into the ascertainment of either (1) a cheap process of precipitating the dissolved matter, including any free acid, or (2) a suitable process for purifying the water.

2. Three theories have been advanced to account for the fixing of dyes by fillers. Results favour the absorption theories of Pelet and Rohland rather than the chemical combination theory of Suida, but discrepancies have been observed in all cases.

3. The success which has attended scientific progress in refining petroleum is the cause of the high cost of gas oil. It must soon render necessary extensive scientific research in the gas industry. *Journal of Industrial and Engineering Chemistry*, vii., No. 6.

ON THE CONDENSATION PRODUCTS OF PHENOL AND FORMALDEHYDE, ESPECIALLY ON BAKELITE.

By GORO MATSUMOTO, Kogakushi.

THE author classified the various condensation products of phenol and formaldehyde into three groups, viz., 1, crystallisable; 2, soluble and fusible; 3, insoluble and infusible products. He made a series of experiments on the conditions of formation of so-called bakelite, one of the products of the third group above mentioned, the results of which are summed up as follows:—

1. The whole process may be divided conveniently into three stages—1, the initial condensation; 2, the concentration of the products; 3, the hardening. Reactions in all stages are greatly accelerated by a small amount of certain reagents.

2. Formaldehyde, which combines with phenol in the initial condensation, can be well estimated by Lemme's method.

3. The following reagents can be used as condensing agents:— H_2SO_4 , HCl , NH_4OH , hexamethylenetetramine, C_6H_5 , NH_2 , Na_2SO_3 or Na_2CO_3 . NaOH is the best. Neutral salts have no condensing effect.

4. As a hardening agent only basic substances, such as NaOH or NH_4OH , can be used. Of these the latter is the better.

5. If NaOH is used as a condensing agent and NH_4OH as a hardening agent, best results are obtained both as to the yield and the properties of the products, so that this combined method is recommended.

6. If cresol is used instead of ordinary phenol an analogous substance is obtainable.—*Journal of Chemical Industry* (Tokyo), xviii., No. 207.

The Faraday Society.—A General Discussion on "The Transformations of Pure Iron" will be held on Tuesday, October 19, 1915, at 8 p.m., at the Institution of Electrical Engineers. The President, Sir Robert Hadfield, F.R.S., will preside over the Discussion, which will be opened by Dr. A. E. Oxley, of Sheffield. Tickets may be obtained from the Secretary of the Faraday Society, 82, Victoria Street, S.W.

RADIOMETRIC MEASUREMENTS OF THE IONISATION CONSTANTS OF INDICATORS.*

By E. J. SCHAEFFER, M. G. PAULUS, and HARRY C. JONES.

THE radiometric measurements recorded in this paper were made with a very sensitive radio-micrometer and a grating spectroscope. The spectroscope is well known to the chemist, but its use in connection with the radio-micrometer has not, as yet, found an extensive application to the study of chemical problems. This is perhaps due in part to the difficulty in constructing a sensitive and easily controlled radio-micrometer. By means of the grating spectroscope and radio-micrometer, it is possible to study quantitatively chemical reactions involving colour changes, and even those not involving such changes, if there are absorption bands in the invisible regions of the spectrum. It will be seen that accurate determinations of very small concentrations of coloured components in solutions can be made very rapidly even when two or more such components are present. The structure of the solvent bands, and time reactions, are a few of the many other important chemical problems which may be investigated by means of this radiometric apparatus.

Purpose of this Investigation.—In connection with some problems now under investigation in this laboratory, it was desired to secure accurate measurements of the hydrolysis constants of certain salts. The spectroscope and radio-micrometer suggested the indicator method, which is based on the changes in the transmission of light by solutions of indicators when varying amounts of hydrogen or hydroxyl ion are present. It will be shown that by means of these changes concentrations of very small amounts of hydrogen and hydroxyl ions can be determined. The method obviously involves a knowledge of the ionisation constant of the indicator as an acid or as a base. A comparison of the ionisation constants of the indicators obtained by several investigators showed that the recorded values varied widely, not only with different methods but with the same method. The results for phenolphthalein in particular show how inaccurate is our knowledge concerning the ionisation constant of that important indicator. Salm (*Zeit. Phys. Chem.*, 1907, lviii., 492) gives the value 8×10^{-10} ; McCoy (*Am. Chem. J.*, 1904, xxxi., 503), 0.8×10^{-10} . In many cases the results of an individual investigation vary as much as 300 to 400 per cent. A. A. Noyes (*Journ. Am. Chem. Soc.*, 1910, xxxii., 858) has applied the theory of indicators to volumetric analysis, making use of the ionisation constants of the various indicators. He expresses the opinion that our knowledge of the ionisation constants of the indicators is for the most part inexact, and needs to be supplemented by further careful investigation. Stieglitz (*Journ. Am. Chem. Soc.*, 1903, xxv., 1126), McCoy (*loc. cit.*), and Salm (*loc. cit.*) have also recognised the importance of such a study. McCoy, Salm, and in particular Noyes and Bjerrum (*Ahr. Versamm.*, 1914, i., 21), have already applied the indicator constants to some of the more important problems which the chemist must face in titrating weak acids and bases; and they have shown in certain cases the extent of the error involved in such titrations. It will then be readily seen that it is important to know the ionisation constants of the more important indicators, especially of methyl-orange and phenolphthalein. In view of these facts, and the value of such ionisation constants in many other lines of work involving the use of indicators, it was decided to make a radiometric investigation of this problem. Methyl-orange was first studied, and a method was developed through the application of Beer's law, which readily gave the concentration of the yellow azo-base and that of the red quinoid ion. Knowing these values and the hydrogen ion concentration, the hydrolysis constant of methyl-orange

* This investigation was carried out with the aid of a grant from the Carnegie Institution of Washington generously awarded to H. C. Jones. From *Journal of the American Chemical Society*, xxxvii., No. 4.

can be readily calculated. The method employed is different from, and was worked out independently of, any other method thus far used in investigating this problem.

Historical.—The results of a number of preliminary investigations on the ionisation constants of various indicators were published in 1904. McCoy (*Am. Chem. J.*, 1904, xxxi., 503), like most of the other investigators who studied this problem, worked colorimetrically, the intensity of the colour being judged by the eye. McCoy employed Nessler tubes for this purpose, while others made use of special colorimeters to determine the amount of indicator transformed into its salt by varying amounts of hydrogen or hydroxyl ions. Tables showing roughly the hydrogen ion concentration at which a large number of indicators undergo change in colour, have been published by Friedenthal (*Zeit. Elektrochem.*, 1904, x., 113), Salessky (*Ibid.*, 1904, x., 204), Fels (*Ibid.*, 1904, x., 208), and Salm (*Ibid.*, 1904, x., 344). Nearly all of the early investigators utilised the principle that the ionisation constant of an indicator is equal to the hydrogen ion concentration at which it is one-half transformed into its salt (see Salm, *loc. cit.*, and A. A. Noyes, *loc. cit.*). Salessky, and later Salm, determined the concentration of the hydrogen ions at this point by means of the hydrogen electrode. Criticisms showing how inexact most of these methods are will be found in the separate articles. Salm (*Zeit. Phys. Chem.*, 1907, lvii., 490), referring to the work previous to 1907, says that the investigations have been for the most part qualitative, and that with few exceptions the dissociation constants of the indicators are still unknown. Salm made a more careful investigation, employing a satisfactory colorimeter to determine when the indicator was one-half transformed into its salt, and like Salessky obtained the hydrogen ion concentration at this point by means of the hydrogen electrode. The results which he obtained with phenolphthalein illustrate the uncertainty of the values found by his method. Wegscheider (*Zeit. Elektrochem.*, 1908, xiv., 510) proceeded in much the same manner as the others who have used the colorimetric method, and obtained constants for the ionisation of phenolphthalein which seem to be in fair agreement with those found by Hildebrand (*Ibid.*, 1908, xiv., 351). Hildebrand's method, involving the use of the spectro-photometer for the estimation of colour intensities, is the most exact of all the methods previously employed. His photometric method somewhat resembles the radiometric method which we employed. Rosenstein (*Journ. Am. Chem. Soc.*, 1912, xxxiv., 1117), following essentially the procedure of McCoy, has carried out very carefully a colorimetric investigation of the ionisation constant of phenolphthalein, and the effect upon it of neutral salts. He employed the Duboscq type of colorimeter to determine the fraction of the indicator transformed by a known hydrogen ion concentration. As he shows, the ionisation constant is equal to the hydrogen ion concentration times the fraction of the indicator transformed into its salt. When the indicator is a fairly strong electrolyte, e.g., *p*-nitrophenol, its dissociation constant was determined by the conductivity method.

Before we can judge of the absolute value of the results obtained in any radiometric investigation, it is necessary that the radiometric instrument, and the other parts of the apparatus used in connection with it, fulfil several requirements. What these requirements are will be taken up in the discussion of the apparatus which follows. In view of the fact that radiometric apparatus has not been extensively used by chemists, it seems desirable that this be discussed in some detail.

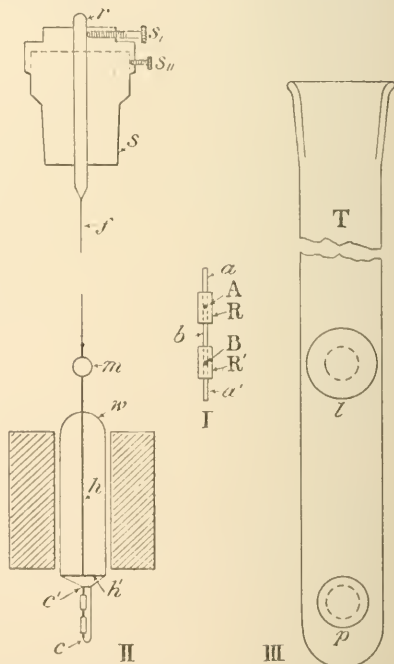
The Radio-micrometer.—The methods employed in the construction of the radio micrometer and especially of the thermo-junctions, we owe to Prof. A. H. Pfund (*Phys. Rev.*, 1912, xxxiv., 228; *Phys. Zeit.*, 1912, xiii., 870). By means of these methods we were able to build a very satisfactory instrument.

The radio-micrometer previously constructed by Guy

(publication of the Carnegie Institution of Washington, 1913, No. 190, 30) was found to be unsatisfactory for use with the grating spectroscope. Its sensibility, according to a recent test was 2 per sq. mm. of exposed vane, candle and scale being at a metre's distance. The full period of this instrument was, however, very short, it being eight seconds. His radio-micrometer could have been made about as sensitive as the one constructed for this work, by using a longer and finer quartz fibre, and making the full period about twenty seconds. However, due to the fact that this instrument was not equipped with a compensating junction, and that its drift, due to this cause, had proved so troublesome in the work of the previous year, it was decided to construct a new radio-micrometer.

Briefly, the radio-micrometer consists of a thermo-electric junction attached to a loop of non-magnetic wire. The whole system is suspended by a quartz fibre in a glass tube. A strong magnetic field surrounds that portion of the tube enclosing the loop of wire. Radiant energy falling upon the blackened junction is converted into electrical energy. In proportion to the amount of energy received by the junction, the suspended system turns through a definite angle in the magnetic field, the loop tending to set itself at right angles to the lines of force. The deflection or turn is given by means of a mirror attached to the suspended system.

The essential parts of the radio-micrometer are shown in the accompanying sketch. Fig. 1. represents the type of compensating junction which was constructed and used.



It is fastened to the loop of copper-wire *w* at *c* and *c'*, as shown in Fig. 11. To support the loop of wire small glass rods are placed at *h* and *h'*. A light mirror is attached to *h* at *m*. A quartz fibre, *f*, is fastened to the end of the glass rod *h*, and to the brass stopper *s*. The whole system is then set in the glass tube *T*, having two windows *l* and *p*. The lens *l* focuses the reflected light from the mirror *m*, on a glass scale. At *p* is inserted a plane glass window 1 mm. thick. The beam of light which is to be measured passes through this window before falling on the junction. The magnetic field is placed between *l* and *p*.

The wire loop was made of a very fine specimen of No. 36 copper wire, furnished by Leeds and Northrup.

Pure nitric acid was used to dissolve the exterior surface of the wire, which was very likely to be contaminated with various magnetic materials. That this wire must have been very pure is shown by the behaviour of the completed instrument. As regards purity, a still better specimen of silver wire was obtained from Weston; but unfortunately none of the junctions attached to this silver wire were sufficiently sensitive for our purpose.

The alloys used for the construction of the thermo-junction were of the composition recommended by Hutchins (*Sil. Journ.*, 1894, xlviii., 226). Fig. 1. of the sketch gives an enlarged view of the junction. It will be noticed that it consists of two thermo-electric junctions A and B, which compensate each other. When the same beam of light falls on both junctions, each sends equal amounts of electrical energy through the loop of non-magnetic wire w , but in opposite directions. Hence, it follows that for exact compensation there should be no turn of the suspended system. In actual operation the beam of light energy which is to be measured is focussed on one of the junctions. This arrangement of junctions is quite essential in any sensitive radio-micrometer where a constant zero point is required; and it is only in this way that the effects of temperature changes and stray sources of light can be eliminated.

The two arms represented by a and a' in Fig. 1., have the composition 97 parts bismuth and 3 parts antimony. The composition of b is 95 parts bismuth and 5 parts tin. These metals are quite pure, and the strips used are very thin. Junction A is formed by sealing strip a to strip b , and junction B is formed by sealing strip b to strip a' . R and R' are the receiving surfaces, or so-called vanes, cut from very thin tin-foil, and soldered to junctions A and B, respectively. These vanes each have an area of 4 square mm., and are coated with lamp-black to prevent radiation of light energy. It was found that the action of an acidified solution of antimony chloride on the tin-foil produces a black receiving surface. Theoretically, it appears that such a metallic receiving surface should be more effective than lamp-black. However, none of the junctions having the antimony receiving surface were sufficiently sensitive to determine whether or not its use is to be preferred to that of lamp-black. Greater sensibility can be obtained with a single junction than with a compensating one, since in the former we have but one seal and two metal strips. This follows from the fact that the sensibility of the radio-micrometer is materially increased when the resistance of the junction is made more nearly equal to that of the wire loop. However, the advantages to be derived from the compensating type of junction are well worth the sacrifice in sensibility.

It is very important that the weight of the junction be kept as small as possible, not only to lessen the weight of the suspended system, but especially to reduce the heat capacity of the junction to a minimum. A small heat capacity ensures a quick acting suspension, and one which will more rapidly return to the zero-point. That the mass of material in the junction is very small can be seen from the fact that the actual weight of one of the completed compensating junctions was 2.9 mgrms.

The quartz fibre was obtained from molten quartz by means of a bow and arrow arrangement. (Dr. C. W. Hewlett has very kindly supplied us with several satisfactory fibres). The total length of this fibre is nearly 30 cm. A long fibre materially aids in eliminating vibrations. This is most essential, especially when the work necessitates small deflections. The period and sensibility of the radio-micrometer depend in a large measure on the proper selection of the quartz fibre.

The plane mirror m (Fig. II.) is very thin, and has an area of about 20 sq. mm. Directly in front of it is the lens l , having a focal length of 12 feet. By means of this arrangement the image of a lamp filament could be sharply focussed on a glass scale about 12 feet distant from the mirror, and it is on this scale that the deflections as given by the radio-micrometer are noted.

The torsion-head stopper s , made of brass and tightly ground into the glass tube T , serves the purpose of making adjustment. By means of it, the suspended system can be made to occupy any position in the magnetic field, and the whole system can be raised or lowered without danger of breaking the very fragile suspension. The torsion-head stopper contains a brass rod r and the two screws s_1 and s_{11} for making the above adjustments.

The glass tube T in which the whole system is suspended is about 45 cm. in length. To it is attached the lens l previously referred to, and the glass window p , through which the beam of light is directed either to junction A or to junction B.

The glass tube surrounding that portion of the suspended system to which the thermo junction is attached was insulated from temperature changes and air drafts by a layer of fine lead shot and wool fibre. To prevent stray sources of light and air drafts from reaching the radio-micrometer, it was enclosed in a wooden box covered with painted canvas.

That the image on the scale should remain steady at a focal distance of 12 feet, it is necessary to shield the radio-micrometer very carefully from the usual vibrations of the building. The long quartz fibre aided materially in this respect. Between the levelling stand of the radio-micrometer and the base on which it rested, various insulating materials were introduced at six points to absorb vibrations.

The completed radio-micrometer, candle and scale being at a metre's distance, gave a deflection of 20 cm., the half-period being nearly ten seconds. In making this determination of the sensibility of the instrument the radiation was passed through a glass window 1 mm. thick, and the tube containing the suspension was not evacuated. Evacuating the tube and passing the radiation through a rock-salt window would increase the sensibility about six times, and the period would become somewhat shorter. Since the receiving vane has an area of 4 sq. mm., the sensibility per sq. mm. of exposed vane is *five*, and the full period *twenty* seconds. When making this determination, owing to the difficulty of properly shielding the junction not in use but serving as compensator, it is thought that the value of *five* for the sensibility is somewhat low. Practically every junction that was tested showed that the sensibility was approximately one fourth of the whole period in seconds. The sensibility value as given by the candle has but little meaning, owing to the varying intensity of the light emitted. The light from the Nernst glower burning at 0.8 ampère and 120 volts, dispersed into the visible first order spectrum 6 inches long at slit s_1 of the spectroscope, gave at $\lambda = 0.95\mu$, a deflection of 250 mm. when focused on the junction of the radio-micrometer. Both slits are 1 mm. in width, and the scale 12 feet from the mirror. Considering the high resolving power of the grating, it will be seen that our radio-micrometer is very satisfactory both as regards sensibility and period. It enabled us to make quantitative measurements of radiant energy from $\lambda = 0.4\mu$ to $\lambda = 2.0\mu$.

For the same source of light energy the radio-micrometer always gave the same deflection and returned quickly to zero, showing that our efforts to eliminate magnetic materials from the wire loop had been very successful. The conduct of the completed instrument has demonstrated that the suspended system is very free from paramagnetic disturbances. The diamagnetic materials composing the junction were all arranged at right angles to the lines of force of the magnetic field, and in this way diamagnetic disturbances were reduced to a minimum. The use of the radio-micrometer has shown that the heat capacity of the junction is sufficiently low to be within the desired limit. The compensating junction and its insulation from temperature changes practically removed any drift of the zero-point. The zero-point for weeks at a time would not drift more than 10 cm. on either side of the zero. In case there was any drift during the measurements it was always very slight, and the proper correction

could easily be applied. The insulation from vibrations made the reflected beam upon the scale fairly steady, even when there were rather violent disturbances in the building. There is every reason to suppose that the scale could be read to about one-quarter of a millimetre when the building was quiet. Duplicate readings under ordinary conditions nearly always agreed to within 0.5 mm.

(To be continued).

THE WAR AND NEW BRITISH INDUSTRIES.

PALM KERNEL CAKE.

IMPORTANT LIVE STOCK FEEDING TESTS.

In order to determine the value of palm kernel cake as a food for live stock in comparison with other foods, Sir Owen Philipps, Chairman of the West African Section of the London Chamber of Commerce, arranged for practical trials to be made at a number of agricultural colleges and elsewhere in Great Britain. The full results of several of these experiments are just to hand, and will be noted with great satisfaction by those interested in finding a market in this country for the palm kernels of the British West African Colonies, which before the war went almost exclusively to Germany.

At the North of Scotland College of Agriculture, for instance, palm kernel cake was compared with linseed and decorticated cotton-seed cake as a cattle fattening food. The animals fed on palm kernel cake thrived equally well with those fed on the linseed and cotton-seed cake. Palm kernel cake, however, gave considerably the best monetary return, the net cost of food per cwt. of live weight increase being in round figures 43s. for palm kernel cake, as against 45s. for cotton-seed and 51s. for linseed cake.

Results obtained in the winter feeding of cattle at the Edinburgh and East of Scotland College of Agriculture indicated that palm kernel cake is a cheaper feeding-stuff than first class Bombay cotton cake, and is practically equal in value to the best class of dried distillery grains. At the Norfolk Agricultural Station results indicated that palm kernel cake is equal in food value to linseed cake, while it is of course much lower in price.

Results obtained at the Agricultural College, Uckfield, Sussex, go to show that palm kernel cake is a better beef producer than Bombay cotton cake. Experiments at other agricultural colleges indicate that palm kernel cake, as compared with other feeding cakes, increases the yield of fat in the milk when fed to dairy cows and gives a gain in the actual milk yield.

Enquiries made by the Imperial Institute, which for many years past has been working to secure the establishment of a palm kernel crushing industry in this country, make it clear that British makers of palm kernel cake are now finding a ready sale for their product. Indeed, the recent increase in the price of this cake (which, however, leaves it still relatively the cheapest cake on the market), is no doubt chiefly due to the desire of the manufacturers to restrict the demand, with which, pending completion of the new palm kernel crushing mills in the United Kingdom, now in course of construction, they find it difficult to cope.

Complete particulars of these latest feeding trials with this cake will appear in the next number of the *Bulletin of the Imperial Institute* to be published this month, and further information on the whole subject of the new British palm kernel crushing industry is given in "Oil Seeds and Feeding Cakes," the first of a series of Imperial Institute monographs just published. Samples of palm kernel cake manufactured in the United Kingdom by the latest improved methods may be inspected in the Public Exhibition Galleries of the Imperial Institute, South Kensington, and the Technical Information Bureau of the Institute will, if desired, supply a list of the manufacturers of the cake in this country.

NOTICES OF BOOKS.

Light and Colour Theories. By JOSEPH W. LOVIBOND. London: E. and F. N. Spon, Ltd. New York: Spon and Chamberlain. 1915.

THIS book contains a description of the methods of colour analysis and synthesis elaborated by the author. The tintometer standards advocated have been used for many years in various industries, such as brewing, tanning, dyeing, &c., and have been found thoroughly satisfactory. After much tedious and lengthy research work the author succeeded in working out a code of laws relating to white and coloured light, of which possibly the most important is the Law of Specific Colour Development, according to which every substance has its own rate of colour development for regularly increasing thicknesses. He describes the method of obtaining the arbitrary unit of colour and hence establishing colour scales which have stood the test of many years' experience.

Identification of Common Carbon Compounds. By J. N. RAKSHIT, F.C.S. Calcutta: The Collegian Office. 1915.

THIS little book contains a collection of tests which can be applied for the identification of the commoner compounds of carbon, and is intended for beginners who have no previous knowledge of organic analysis. It opens with a scheme for the examination of single substances, giving simple chemical and physical tests, and proceeds to give details of the most rapidly performed and characteristic tests for the individual substances. The scheme given for the detection of the various common organic acids seems practical and useful, and the list of substances arranged in order of their melting points will give some clue to the identification of an unknown substance.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxi. No. 9, August 30, 1915.

This number contains no chemical matter.

No. 10, September 6, 1915.

Stimulating Action of Magnesium Salts on Lactic Fermentation.—Charles Richet.—In 1892 the author showed that all the metallic salts, in definite quantities, stimulate lactic fermentation, but the most active are the salts of magnesium. He proved more recently that with increasing quantities of $MgCl_2$ the quantity of acid formed increases up to a certain limit and then rapidly decreases. The optimum occurs at about 12.5 grms. per litre of $MgCl_2 \cdot 6H_2O$, a number which is remarkably close to that found by Delbet for the optimum of phagocytose.

MEETINGS FOR THE WEEK.

TUESDAY, 19th.—Institution of Petroleum Technologists, 8. "The Petroleum Industry of Mexico," by P. C. A. Stewart.

— Paraday Society, 8. General Discussion on "The Transformations of Pure Iron." "Transference of Electricity by Colloidal Particles," by F. Powis. "Electrolysis of Nitric, Sulphuric, and Orthophosphoric Acids using a Gold Anode" and "The Electrolysis of Concentrated Hydrochloric Acids using a Copper Anode," by F. H. Jeffery. "The Thermal Decomposition of Hydrogen Peroxide in Aqueous Solution," by W. Clayton.

WEDNESDAY, 20th.—Microscopical, 8. "A Statement upon the Theory and Phenomena of Purpore and Intelligence exhibited by the Protozoa, illustrated by Selection and Behaviour in the Foraminifera," by B. Heron-Allen.

ERRATUM.—P. 186, col. 2, line 12 from top, for "cb cm." read "sq. cm."

THE CHEMICAL NEWS.

VOL. CXII., No. 2917.

PRESIDENTIAL ADDRESS TO THE SOUTH AFRICAN ASSOCIATION OF ANALYTICAL CHEMISTS.*

By Dr F JURITZ, M.A., F.I.C. (Government Analyst, Cape Town),
President of the Association.

GENTLEMEN,—The honour which you conferred on me a year ago in electing me as your President, in spite of my residing many hundreds of miles distant from the headquarters of this Association, has in my eyes an enhanced value by reason of the fact that at the time of my election I had recently left South Africa for Australia, and realising as you did how impossible it would be for me in any case to attend your Council meetings during my year of office, you nevertheless singled me out for this generous distinction. I highly appreciate the honour, and tender you my sincere thanks.

And now, gentlemen, I have travelled over one thousand miles in order to be with you to-night and to deliver my Presidential Address to you in person, and you on your part have adjourned your Annual Meeting from an earlier date in order to convenience me. I trust, therefore, that under these circumstances you will grant me the privilege of ranging in my remarks beyond the limits of this Association's primary objects and duties. My two predecessors in this chair have dealt with those points so ably that it would be hopeless for me to attempt to equal them. Moreover, you have Dr. McCrae and Prof. Stanley continually amongst you to hold that standard as high as it should be held. They have rightly set before you a lofty aim. I have consequently some excuse for branching out laterally in the course of my remarks, and looking for an extension not of scope but of operations. I do not think that in so doing I shall in any way transcend the bounds which our Association has set itself in its constitution, for the Association's objects as there laid down are as wide as one could wish; they embrace, in addition to other functions, the encouragement and extension of processes which fall within the activities of the technical chemist, to whose ranks in fact my immediate predecessor and several others of our members belong.

In thinking over various topics on which to address you it occurred to me that everything could be reduced to one or other of two heads. There are certain functions which an Association such as this may reasonably be expected to exercise with respect to the science of chemistry and to those who profess it; there are also certain functions which the State—using the term in its widest sense as including the general public—may not unreasonably be expected to exercise towards the chemical profession. Along these two lines of thought I shall endeavour to crystallise my ideas, of course without any attempt to be at all comprehensive.

It will be convenient first to consider the latter theme—the analytical and consulting chemist in his relation to the State.

What a change has come over the world in the brief year since this Association held its last annual meeting! Yes; but all that which we see and feel to-day has been banking up—has been latent—for years. When I say this I do not allude only to the political aspirations of Germany, nor even to the manner in which that country has pressed chemical science into unprecedented and un-

anticipated service. A member of this Association observed to me not long ago that Britain is suffering in this war because of her neglect of chemistry for the last score of years. The man in the street will be apt to ascribe the utterance of such a sentiment to sympathy with Germany's ambitions and methods, but the British chemist will be inclined to shake his head sadly at such an ascription.

Three years ago in my Presidential Address to the Cape Chemical Society I quoted some plainly spoken warnings given by Prof. Meldola and by Prof. Kipping contrasting the position of chemical research in England unfavourably with its condition in Germany, and in his Presidential Address to the Institute of Chemistry four months ago Prof. Meldola administered to the people of England a reproof for failure to recognise and utilise the results of chemical research. He said:—

"It is absolutely painful that under the stress of circumstances our weakness should have been laid bare to all the nations, a weakness for which there can be found no justification in the plea that no alarm had been raised, or that the supply of chemical talent in this country was inadequate."

At a later stage of his address, speaking about the anxiety that was being manifested as an outcome of the war to see the coal-tar colour industry restored to England, he said:—

"The German colour industry has been built up by the utilisation of the results of research carried on in the factories and universities and technical schools for a period of over forty years! To suppose that we can retrieve our position after forty years of neglect by starting a company the directorate of which is to consist solely of business people is simply ludicrous."

In analogous terms Dr. W. H. Perkin, bearer of a name illustrious through its identification with the discovery of the aniline dyes sixty years ago, refers to the position of the organic chemical industry in his Presidential Address to the Chemical Society in March:—

"The manufacture of organic colouring matters during the critical years 1870—80 was, owing to the neglect of organic chemistry by our universities, placed in a practically impossible position"; and, on the other hand, "it may indeed be said that Germany has no competitor worth considering in the whole domain of organic chemical industry" (*Journ. Chem. Soc.*, April, 1915, 558).

In the *Chemist and Druggist* of April 10 we read:—

"France, like England, has allowed Germany completely to outstrip her in chemical research and industry, and one of the chief reasons given by M. Barthe is the same that has been alleged here, namely, the miserable salaries paid to trained chemists—when, that is, they are lucky enough to earn any salary at all."

The highly distinguished editor of the *CHEMICAL NEWS* some weeks ago took occasion to publish a leader on "Science and the State," whereof a few of the closing sentences were particularly trenchant (*CHEMICAL NEWS*, April 30, 1915):—

"The results of the German methods of scientific education," said he, "have certainly been the production of men of resource, who are able to act promptly and on their own initiative in emergency, such as we appear to lack at the present crisis. . . . It is perhaps not too much to hope that now England will really begin to wake up, and no longer be content to be outclassed in the future as she has been in the past, owing to the mistaken policy and supineness of her statesmen and educationalists and to the insularity of her people."

Sir William Crookes in the same editorial laid stress on two duties which science owes to the State. One is readiness to give her services freely, "and this duty," he rightly added, "has never been shirked." But then, "in return for its services to the State, science has a right to look for more recognition on the part of the Government, greater scope for its activities, and more prospects of obtaining good remuneration, so that the scientific man may

* Delivered at the Annual Meeting, held at the School of Mines, Johannesburg, July 9, 1915.

be able to pursue his work free from anxiety about ways and means for himself and his dependents."

If, then, the State is to get the best out of science at a period of national crisis, she must also do her best to foster scientific study and scientific profession when times are normal. It is blind folly alone that can starve the goose which lays golden eggs.

But, so far from giving the chemist his due recognition, the State as a rule receives his gifts rather unappreciatively, if not indeed ungraciously, and accordingly there arises the second duty which science owes the State, and by far the harder one, the duty of educating public opinion on the subject.

"The classically trained statesman," says Sir William, "would probably be able to state clearly some of his views on the debt the world owes to Shakespeare, but he would in all probability be quite unashamed to admit that his knowledge of the achievements of Faraday was almost non-existent."

One might considerably extend the evidence afforded by such quotations, but let me just close the case by referring you to the address recently given before the Institution of Chemical Technologists by its President, Col. C. E. Cassal, V.D., in which he recalled warnings regarding the condition of British chemical industry that had been uttered by Prof. Green in 1901 before the British Association, and by the late Sir William Perkin before the Chemical Society in 1885. The latter asserted that the success of the German chemical industries was due to the employment of high-class professional chemists, and so, Colonel Cassal asked, what steps do our manufacturers take and what steps do our Government authorities take to encourage the high-class chemist? By way of answer he proceeded to quote an advertisement by a British Government Department for an accurate analyst, university graduates or members of the Institute of Chemistry preferred. "Wages"—yes, that was the word used—"wages, £2 os. 6d. per week." "If a Government Department sets such a scandalous example, what," asked Colonel Cassal, "is to be expected from the ordinary manufacturer?"

What a picture these quotations reveal! Chemical institutions dominated by purely business men, important branches of chemical science ignored by the universities, the chemical profession skimmed and starved, and the gifts it bestows unappreciated. In my address of three years ago I quoted Prof. T. Edgeworth David, of Sydney University, as saying that if Great Britain is behind Germany in these respects Australia is behind Great Britain, and I expressed the fear that South Africa is just as truly behind Australia. I have since visited Australia, and I do not fear any longer—I know!

Let me take you for a moment to the United States of America. Three months ago the American Chemical Society held its fiftieth annual meeting at New Orleans, and the President of the Society in his address sought a reason for, as he expressed it, "Germany's supremacy in most of the branches of chemical industry." The reason he found was that "German chemical enterprises are run and managed by chemists," not by merchants, lawyers, or bankers.

"The fault," said he, "is not with the American chemist, nor with his ability, nor his willingness; the fault lies principally and almost wholly with those in charge of many of our industrial enterprises, who fail absolutely in a chemical understanding of their own products, and are devoid of any sympathetic contact with chemistry and with chemical points of view, and therefore are incapable of and unable to appreciate the value of chemical work, or to have a wholesome understanding of the snares, the pitfalls, and the tedium of chemical research" (*Science*, 1915, xli., 672).

It is not a little remarkable that the *Journal of Industrial and Engineering Chemistry*, published by the American Chemical Society, has in its April issue a symposium of no less than twenty articles, whose united object is to

demonstrate what chemical science has done for the country's industrial development. It is worth while running over the list of titles of those papers. They deal respectively with the contributions of the chemist to the wine industry, the copper industry, the coin products industry, the asphalt industry, the cotton-seed oil industry, the cement industry, the sugar industry, the incandescent gas mantle industry, the textile industry, the fertiliser industry, the soda industry, the leather industry, the flour industry, the brewing industry, the preserved foods industry, the potable water industry, the celluloid and nitro-cellulose industry, the glass industry, the pulp and paper industry, and the coping of the whole symposium is the Presidential Address on "The Contributions of the Chemist to the Industrial Development of the United States." If we ask what train of circumstances was responsible for this symposium, the reply is, the war. An editorial in the same issue begins thus:—

"A discovery of enormous potential importance to the chemical profession has been made within the last few months by the general public. Hundreds of newspapers and periodicals are devoting editorial space to the discussion of the chemists and chemical engineers and their relations, and especially their obligations to the coal-tar dye industries."

Let me press home one point that our American *confrères* are realising, for it is a point which we as an Association and our members as members of a particular profession should not only realise but also act upon. It is thus put in the editorial just quoted from:—

"Every worker thrives upon public recognition of his achievements. The chemist is no exception to this rule, yet, from the obscure and involved nature of his work, and his natural secretive instincts, he has received less public acknowledgment than the workers of any other profession."

... We have laboured for years under cover. Is it any wonder, then, that we were still undiscovered when the foreign crisis disclosed to the public the fact that some of our great industries depended for their development and continuance upon the work of the chemist? ... The time seems ripe for coming out into the open and showing the public in clear and authoritative form the place of the chemist in industry."

Speaking as I am in Johannesburg, in the very midst of the biggest gold-mining industry in the world, an industry whereof chemistry is the very pith and marrow, it seems almost amusing that one should need to emphasise the importance of the chemist to the development of a country's industries; yet remember, away from the Rand the works chemist is virtually an unknown quantity in South Africa, and for the most obvious reason—that the chemical industries which call him into being in the world's older countries are non-existent. That is so partly because some of those industries would have no materials to feed on here and no local needs to meet. Naturally the country cannot support industries of a type for which she is not yet ripe or suited, but there are industries of other types which if they could only be got going would find adequate support, and the cause of their not getting going may be lack of confidence or lack of energy or lack of knowledge.

I daresay the industry in South Africa that approximates nearest to that of gold extraction, in the employment and training of technical chemists, is that of the manufacture of explosives, closely associated with which are such processes as the production of sulphuric acid, of sulphur for agriculturists, and of certain insecticides, calcium arsenite for example. It is interesting and encouraging to observe how an industrial works like a dynamite factory gradually adds to its prime function, impelled thereto first by its own needs and thereafter by openings for the utilisation of its by-products, one subsidiary industry after another. I am not indisposed to lay down the principle that the Government, which offers cheap rates for transport of agricultural produce and fosters the agriculturist, very properly, in various ways would be acting on most sound

lines if it were to offer analogous advantages to chemical industries. I have already admitted that there are some chemical industries that cannot find standing ground in South Africa, but there are others that even now occupy fairly strong positions, and that would not find much difficulty in extending their scope. If the Government, either by the bonus system or in other ways, were to hold out inducements for such extension encouragement would be afforded for further development of branches of chemical technology in the Union, and the country would benefit indirectly as well as directly. For instance, I have mentioned the manner in which the explosive factories already aid the agriculturist; there are other ways in which they can do this, and the Government by encouraging an extension along those lines would at the same time be aiding the farmer. Just one illustration of the direction in which such extension might proceed:—From the production of sulphuric acid to the manufacture of superphosphates is but a step. I am not aware that any superphosphates are made in this country, but huge quantities are imported, and at the same time all over the Union an enormous waste of bones is continually taking place. If the collection of all these bones could be organised and their transport to the places where sulphuric acid is made facilitated much will have been done in the direction of reducing the importation from overseas of an article which we should be able to produce locally.

The mention of superphosphates reminds me that, principally in Natal, factories for the production of fertilisers already exist in South Africa, and these constitute the third class of factories that afford scope for the technical chemist in the sub-continent. These, too, may well widen their scope, especially nowadays, when some of the material which I gather they have all along imported from abroad has ceased to be procurable. The war has rendered the usual sources of potash fertilisers perfectly inaccessible, and South Africa needs these as much as any other country does. During the last few days I have addressed the South African Association for the Advancement of Science in regard to the accumulations of large quantities of sheep manure and sheep manure ash, relatively rich in potash, which are to be found practically as a waste product over a large part of the Union. And while we speak of waste as well as of potash I would once more draw attention to the fact that within the Municipality of Cape Town alone some 1500 tons of seaweed are buried annually as mere refuse, and this at a time when one reads in all the scientific periodicals of the revival of the kelp industry. Previous to the discovery of the Stassfurt salts seaweed ash used to be largely employed for the preparation of potash, and Heiden ("Coprolology," ii., 417) states that *Fucus nodosus*, common on the South African coast, yields an ash with a potash content of about 20 per cent, while Lundie and Hallack, at the South African College, found 30 to 40 per cent of potash in the ash of species of *Fucus* from Sea Point and False Bay. As long as the war lasts the only important source of potash available will be seaweed ash, and this article, which has been rising in value since the war began, is being consistently disposed of with all possible speed by the municipality of which I am a citizen. A ton of kelp will probably be worth about £6 this season, and as it takes five tons of dry weed to make one ton of kelp, the material annually cast up by the tides along the shores of Table Bay is worth about £1800, and that quantity is small compared with the crop awaiting harvesting in the shallows, a crop that renews itself so rapidly that the harvest is practically perennial.

The sheep farmer has other waste products besides Karroo ash which are potential sources of potash. A fleece which weighs 8 lbs. is capable of yielding, by lixiviation, 130 to 200 grms. of pure potassium carbonate, and it has been calculated that 6½ millions of sheep, producing 54 millions pounds weight of wool, will yield annually over 2½ million pounds weight of potash, representing a money value of £80,000, and that over a quarter of a

million pounds sterling was the value of the potash imported into England in wool from Australia and the Cape during a single year (Wagner, "Chemical Technology," transl. of 8th ed., 1872, p. 132).

Another chemical industry in South Africa in connection with which technical chemists are employed is the production of soap, for which factories are in operation near Cape Town, in the province of Natal and elsewhere in the Union. Here, again, there are welcome indications of the establishment of subsidiary industries, for it is understood that in connection with some of these factories oil-cakes for cattle feeding are being manufactured. Nor are soap factories the only institutions in the country where oils form the basis of commercial products. As an adjunct to the work of the Government guano islands it seems as though a prospect may open for the utilisation of the seal oil, which is now almost a waste product. Yet another industry has taken shape in the whale fisheries which have dotted themselves right round the coast, from east to west. In some localities they too have an adjunct, namely, fertiliser works, and it is imaginable that as an outlet for the whale oil subsidiary soap works may be established in this connection also, and use may be found for the product of these works in the direction of locust destruction.

Then we have the viticulturist and the dairy farmer, who have each, by aggregating themselves into co-operative societies, made openings for chemists to aid and advise such bodies. And, lastly, we have the cane-sugar industry of Natal, which rivals Western Province viticulture in producing alcoholic liquors, mention whereof brings us to a subject which has of late loomed very large in the minds of some technologists, viz., alcohol as a motor fuel, a subject which is assuming vastly increased importance in all the belligerent countries, and to which our own Government has also been devoting some thought.

Now, what does the average South African know of the value of the chemist to the country in respect of industries like those that I have mentioned? Little or nothing, I venture to assert. Why, the whole of this great agricultural country is a spacious natural chemical laboratory, and, as I have so often said, we should make it our first business to study and turn to account the processes that are going on in that laboratory, instead of which we are just frittering away the time and opportunity we have of doing so, through sheer ignorance of the position and function of the chemist in relation thereto. Even in some of the highest places knowledge about the capacities and functions of the chemist is deplorably vague. It is just here that a chemical association steps in and informs all and sundry regarding the scope and work of the profession, and I am most pleased to testify that this Association is already doing excellent educative work of this kind in quarters where it is plainly needed. Some may argue that we are only an association of analytical chemists. True; but our very constitution transcends the limitations of that adjective, or else there is no meaning in the phrase "technical processes depending on chemical knowledge," the knowledge of which processes we are bound by our constitution to encourage and extend.

The very isolation of the chemist in South Africa makes the sort of educative work I speak of all the more needed here. A chemist following his profession in South Africa labours under disadvantages of a character scarcely conceivable by a *confrère* who has never left Europe. Most of these cannot be removed by his own unaided efforts; hence the need of an association. It is perfectly fitting that such an association should have its headquarters in the midst of this busy hive of chemical industry; no other locality is conceivable. Here in Johannesburg, in addition to the Association over which I now have the honour of presiding, you have that very flourishing institution, the Chemical, Metallurgical, and Mining Society of South Africa, in your immediate vicinity. We, on the other hand, who inhabit what has

been somewhat unkindly termed the shank-end of South Africa, have so few chemists in our neighbourhood that it has been a matter of extremest difficulty to keep our one little chemical bantling, the Cape Chemical Society, alive during the nine years of its past existence. Indeed, I am not at all sure that it would not be wise to merge that Society in this Association and constitute it a branch thereof, having its special venue in the Cape Province. Such a course would, for the Association, have the advantage of adding to its roll an appreciable number of new members, as well as a pecuniary nest egg; for the profession it would carry the weight of this Association's directing and controlling influence into a part of the country where it is at present practically non-effective, and on the public it would confer the benefit of a live and watchful guardian of their interests in a province where there have been in operation for several years three distinct adulteration laws, embracing within their scope, in addition to foodstuffs in general, particularly wines, beer, spirituous liquors, and vinegar, and also fertilisers, feeding stuffs for cattle, and insecticides or pest remedies.

To the amalgamation indicated one objection may be founded on the differentiation between chemists and analysts. This Association, as I have just observed, is an Association of analysts. Now, of course, every analyst is, or should be, a chemist, but every chemist is not an analyst. A teacher of chemistry, or a consulting chemist, or a works chemist may feel himself quite at home in a "Chemical Society," but out of place—if the distinction be very strictly insisted on—in an "Association of Analysts," even though the latter term be writ large as "Analytical Chemists." The feeling of such may be that if the operations of our Association were so widened as to embrace, not merely the supervision of the professional interests of chemist from a business point of view, but also the ventilation and discussion of the purely scientific aspect of the work of that most useful, but often maligned, and more often misunderstood body of men, they would see their way open to being numbered within its ranks.

It may be argued that the function of presenting chemical papers is well performed by the Chemical, Metallurgical, and Mining Society of South Africa. But, after all, in that abode chemistry has to sleep three in a bed, and when she shows herself she always appears clothed in a miner's garb. The foods chemist, the agricultural chemist, the student of physical or of organic chemistry have no medium under the ægis of their own profession for the exchange of views. Moreover, solidarity and not diffuseness is what chemical science needs, if there is to be any speaking on behalf of the profession, either to the public or to state officials, or, as this Association occasionally does, to individual members of the profession who need the guiding rein.

Above all, solidarity is requisite if ever the profession of the chemist in this country is to be an incorporated one, and if the right of calling himself by his scientifically correct title is to be preserved to him, and not transferred, as in England, for the exclusive use of pharmacists. And the chemist needs legal protection in his profession no less than the pharmacist and the physician do in theirs, and a great deal of educational spade work will be necessary before it begins to dawn on people that "chemist" is not synonymous with "apothecary" nor "chemicals" with "drugs."

As Dr. McCrae wisely advised two years ago, Government, corporations, and public sadly need educating with regard to the training and qualifications that constitute a chemist and differentiate him from druggists or pharmacists and medical practitioners, and this education must be compulsory, for, said my predecessor, out of season as well as in season it should be insisted on that qualification for the practice of the profession presupposes adequate training and deserves official recognition. "Life is at stake," is the counter argument, "and therefore the physician and surgeon are statutorily protected." But, if prevention be better than cure, surely the chemist who, by

testing the water supplies—or the milk supplies—of large centres of population, detects contamination betimes, can make out a better case of protection of title than his medical brother. We need only mention illustratively the military operations just outside the borders of our territories, in which the aid of the chemist was sought in determining which water supplies were and which were not poisoned or otherwise unfit for consumption. Instances are, in fact, so abundant that they would multiply in the mentioning.

The prevision of the chemist, furthermore, saves our money as well as our lives. A few years ago one of South Africa's largest cities was saved by the chemist's interposition, from sinking £100,000 in a bubble project, and not long before that the Government of Cape Colony had already proceeded as far as to receive Parliamentary sanction to embark £150,000 in a certain scheme, when the chemist stepped in, demonstrated its un wisdom, and saved the expenditure to the country. The fact is that, placed in a position of equal trust and responsibility, the chemist may, at any juncture, save or lose as much in lives and sovereigns to the nation as the doctor, and yet this one is by law ring-fenced against quacks, and that one is treated as scarcely a professional man, sometimes even ranked with blacksmiths and carpenters, and the science which he professes is dealt with as though a Cinderella among the sciences. Almost all who are not themselves chemists, if they have any conception at all of relative status, settle down on the lees of a prejudice that the chemist moves necessarily on a lower scientific plane than the medical man. Let me say in perfect fairness that my experience of the medical man is that *he*, at least, does not share in this misconception.

Along the lines just indicated a representative association of chemists may make its appeal to the authorities of the State. Now, what about an appeal to the man in the street? You will remember my quotation from the *American Journal of Industrial Chemistry* that the chemist labours too much under cover, and ought to come out into the open. This is requisite in the interests as much of the public as of the chemist himself. Consider only the matter of the purity of food, a matter in respect of which we must not wait for the Government to give us a lead. Ten to twenty years ago Quarterly Reports of the Cape Laboratories, on work done under the Cape Food and Drugs Act, used to be published in the Government *Gazette*, and furnished themes for many a racily written leader in the public press. And these were not void of salutary effect on sophisticators. That is about the length of the Government's tether outside of the law courts. But for years those reports have ceased to be published, and the public now learns little concerning much excellent work that is being done. What, then, can the Association do? One of its objects, as defined by its constitution is the extension of "the knowledge of the nature and composition of commercial products." The Institute of Chemistry of Great Britain and Ireland, in furtherance of a similar object, has published at intervals during the last three years, a series of lectures on such subjects as "Cellulose," "Cement," "Explosives." I do not anticipate that we shall organise such lectures, much less send forth such publications, for a long time to come, but we aim also at encouraging and extending the knowledge of the manner in which those commercial products are adulterated. To this extent, then, we may follow in the wake of the Institute of Chemistry: it may occasionally be possible to arrange experimentally illustrated lectures on such subjects as food adulteration. Members of the staff of the Cape laboratories have given lectures of this type, both in Cape Town and its suburbs, and at Grahamstown, and they instruct and impress those who hear them even more than a press report or a racy editorial.

We should unquestionably gird ourselves to the adoption of an educative policy, for until that is done on well defined lines we shall achieve little else. To my mind some of the points in our propaganda should be:—To

urge reciprocity of benefit between the State and the chemical profession; to demonstrate to the public its indebtedness to the industrial chemist; to seek unity of effort as a profession in all our aspirations; to hasten the incorporation of the chemical profession; to enlighten the public especially with regard to food products and their adulterations. If this Association sets itself steadily to initiate this programme during the next twelve months it will be taking a very marked step forward along the highway of service not alone to the chemist, but also to the State.

NOTES ON PLANT CHEMISTRY.

By P. Q. KEEGAN, LL.D.

Canary-grass (Phalaris arundinacea).—This reed-like organism, though not a native of this realm, rears a dainty company of tall spears by the edges of rivers, streams, and ponds, or in the shady thickets of marshy woodlands. As it has close affinities with the rice plant of the eastern tropics, it is here selected for analysis in order to illustrate as far as possible the phenomena of grassy vegetation. Systematically it is a member of a tribe intermediate between the series Paniceæ (finger-grass, &c.) and the Poaceæ (vernal-grass, &c.), and like most of these plants it shuns lime soils, as it needs phosphoric acid and ammonia rather than nitrate as a stimulant of growth and a supporter of its special physiological energy, while at the same time it really depends much on a good supply of nitrogen from the soil. On July 28 the leaves dried and bruised yielded to boiling benzene about 2 per cent wax, with carotin, phytosterol, &c., but no glyceride. The residue of the leaves was dried and boiled twice in water, and these extracts yielded no nitrate, tannin, or alkaloid; there was a little tannoid which by its behaviour with Millon's reagent, AgO, and alkalis was shown to be a kampherol derivative, and not related to quercetin; on the other hand, the reactions of sugar, especially of saccharose, were extremely marked, both in the solution itself and in the mucilage (triticin) precipitated by alcohol therefrom. Further treatment of the leaves proved that they contained no ordinary pectosic mucilage, no reserve starch, and no oxalate of calcium; but, again, there was a powerful indication of another sugar—a pentose this time, which with resorcin-HCl, gave an orange, with molybdate of ammonium a deep blue, and with boiling acetate of aniline a splendid red coloration. The ash of the dried leaves amounted to 7.4 per cent, and yielded 35.7 per cent soluble salts, 37.5 silica, 10.2 CaO, 4.8 MgO, 6.7 P₂O₅, 6.1 SO₃, 12.3 Cl, with about 2 per cent oxides of iron and manganese; there was no soluble carbonate. The above analysis indicates a feeble energy of deassimilation as well as a powerful activity of assimilation as respects certain carbohydrates. The leaf is comparatively broad and flat, has stomata on both sides, and has ample water conducting tissue, so that the water content thereof undergoes brisk changes with rapid reparation. These conditions seem to ensure that the maximum of assimilation is quickly reached in the daylight, a great deal of oxygen is given off by the leaves, and hence they exhibit that specially remarkable vividness of greenery so characteristic of grassy vegetation. These conditions also secure that in many grasses starch is not formed in the palisades at all, but on bright days the parenchyma sheath which surrounds the veinlets are well filled with it but only temporarily, as in all probability, instead of being resorbed as in other plants, it is largely hydrolysed to hemi-celluloses (xylan, &c.). The flowers contained only a trace of carotin, but had a little tannoid and nitrate, much saccharose with some free levulose, and a purplish pigment whose reactions proved that its origin was not similar to that of the anthocyan of flowers; it is more dehydrated and more phlobaphenic like the erythrophyll of autumn

leaves; in any case it is an original coloration and not a derivative of caffetannin. The stout fibrous roots have copiously branched side-roots, and contain no starch, tannin, alkaloid, or glucose, but have abundant pectosic mucilage, nitrate, cane-sugar, and pentosan; the ash has only 2.8 per cent P₂O₅. The presence of nitrate here raises the question as to whether it is absorbed from the soil or is formed in and by the physiological activity of the plant itself. According to Berthelot the nitrate is not formed in the soil or in manures, but in the stem itself by cells which behave like nitric ferment, inasmuch as it exists in the stem of most plants (10.1 per cent to 2.2 in the rootlets) in such a proportion that it must needs be formed in the tissues thereof and not elsewhere. This opinion has been strongly controverted. But removing from it the postulate of special nitrifying microbes, and estimating the value of the facts that in the canary-grass, &c., there is a poverty of tannins and organic acids, and the nitrogen needed for fructification, &c., has a long way to travel up a rather sparse-leaved stem not over provided with sieve-tube conducting tissue, not to mention that its habitat is ill-adapted for nitrification, &c., I am not fully convinced that Berthelot is entirely wrong. The abundance of phosphates and the great osmotic pressure owing to abundance of sugar would seem to vastly intensify the process of deassimilation leading to the formation of nitrate. "Grasses live by nitrogen from the soil," says Deherain. But says André, "It must be conceded that in the case of siliceous soils a synthesis of nitrogenous matters at the expense of the nitrates is not probable."

Purple Loosestrife (Lythrum salicaria).—This fine plant decorates quite gracefully and brilliantly the tangled mass of vegetation that invests peaty fallows and marshy meadows fringing the stream or pond. It has been regarded as little more than a saxifrage with united styles and scattered stamens, but its true systematic position is near the willow-herbs in the Myrtales alliance. The root is fibrous, branching, of a blackish brown colour, has aerenchyma, and a large quantity of gallotannin. An aqueous decoction of the overground parts of the plant (minus the flower spikes) contained not nitrate or alkaloid, but had mucilage, starch, and glucose, and some free levulose; there was no flavone, and the tannin responded to the tests for gallotannin, but seemed not quite free from traces of catechol tannin, because while it gave the HCl-vanillin and diazonium tests well, that with pine-wood was a failure, and towards alkalis the colorations were fine reds, but no greens or blues like the tannin of the willow-herbs, but unlike that of the blackberry and the rose-root. There was a moderate amount of carotin and a yellow resin, also fat in the chlorophyllian parenchyma; but a special peculiarity was the great quantity of pectosic mucilage and starch extracted by dilute soda and by hot dilute HCl respectively. The ash amounted to 7.3 per cent in dry matter, and contained 25.6 per cent soluble salts, 4.4 silica, 32 CaO, 3.5 P₂O₅, 9.5 SO₃, 4.6 Cl, about three oxides of iron and manganese; there was no soluble carbonate or phosphate. The flowers contained gallotannin and little or no sugar; the anthocyan yielded reactions recalling those of the geranium or rhododendron petals, showing that it was an original red pigment and not an acid blue. The analysis of this plant reveals a considerable intensity of vital energy. The special aerenchyma which surrounds the woody parts of the roots and stem which burrow in the wet soil serves to supply oxygen; hence there is production of the highly oxidised gallotannin, as in marsh cinquefoil, &c. The predominance of root and stem over the leaves is a prominent feature of the plant. The leaves are narrow, and they and the roots were seemingly nearly exhausted of the nitrogen (the leaves had only 9.9 per cent proteid), and phosphorus available for the supply of compounds containing these elements to the reproductive organs, which produce twelve stamens and numerous ovules and seeds. The result of this special facies of

vegetation is the production of a large amount of tannin and oxalic acid. But perhaps much more remarkable is the amount of reserve starch, mucilage, pararabin, and pentosan which suggests the absorption from the soil of a large amount of humic acids or humate of potash (peat contains about 56 per cent carbon) which, after digestion by the roots, would diminish any nitrate present, and induce an active formation of carbohydrates. Altogether this plant displays a very powerful chemical activity, an infallible symptom of a perfect adaptation of anatomical structure to the soil, situation, climate, &c., of the habitat which it embellishes so gloriously.

Heather (Calluna vulgaris).—This eminently natural plant is of slow growth, and lives up to some twenty-seven years. It affects poor and dry siliceous soils, though lime does not exterminate it; a rocky bedding poor in alkalis with a sour humus rich in carbon and of slow decomposition and perfectly free from artificial manure suits it best of all. It has a stout, tapering, finely branched tap root, and does not shoot up a main stem, but only numerous woody branches. The chemistry is very pronounced and of considerable physiological interest. The overground parts are well coated with a suberous layer (cutin with 68 per cent carbon), and have some fat oil and much carotin but not much resin. Quercitrin and myricitrin formerly used for dyeing wool are present in great quantity, and yield reactions of great power and brilliancy. There is also about 7 per cent of a distinctively catechol tannin of a highly chromogenic character recalling that of the Primulaceæ. (The plant is on the borderland of the Gamopetalæ with superior ovaries, and chemically distinct from the most of the rest of this great division). Much starch, gum, pentosans, and oxalate of calcium are freely deposited; a quinol glucoside named arbutin is occasionally present, which indicates a certain connection with the Gamopetalæ; there is very little free sugar or acid of any kind. In May the dried plant contains 9 per cent albumenoid and about 5 per cent at other times. The quantity of ash seems to vary considerably according to season, soil, and situation from 3.2 to 6.3 per cent in dry matter. My own analysis of air-dried materials got in September on a dry rocky locality yielded 2.4 per cent crude ash which contained 31 per cent soluble salts, 21.6 silica, 17 CaO, 8.7 MgO, 8.9 oxides of iron and manganese, 7.3 P₂O₅, 6.5 SO₃, and 2.2 Cl, with very little carbonate. The leaves are of a decidedly xerophilous structure, and live for two or three years; in winter their starch and oil are resorbed, but have more tannin than at any other time. The flowers in high latitudes assume a brilliant purple or bright rose coloration owing to being more numerous with a greater intensity of oxidation and a poorer supply of water. The roots have mycorrhiza; there is no nitrate, there is no abundant storing up of starch, and there is no specially efficient water conducting tissue. In fact, as the number of the vessels in the wood increases their diameter decreases at the same time, so that we have a very xerophilous sub-shrub instead of a tall tree. We have also for this reason the phenomena of a powerful development of physiological and chemical energy encased as it were in a comparatively dwarfed organism. Few shrubs of orders other than the Ericaceæ produce such a battery, as it were, of chemical constituents of high order and reactivity as this "emblem of solitude" displays. The mean breadth of its annual wood rings is only 0.3 mm., which is less than that of the bearberry, a plant of much smaller dimensions and of longer life; while the greatest breadth of its root-neck is lesser still in comparison. Thus, while there is a feeble absorptive activity with an early formation of reserves, i.e., a fixation of immediate principles in the cells, there is no fixation or accumulation thereof in internal glands, which are quite absent in this species.

Ragwort (Senecio jacobæa).—This plant is a member of a vast genus, and is a very fair representative, chemically speaking, of the great order Compositæ. It inhabits dry, rocky, gravelly, or sandy soils, is provided with fibrous

roots specially adapted thereto and with no mycorrhiza, and is also supplied with secretory canals and no latex vessels. On August 1 the dried leaves yielded to boiling benzene 2.4 per cent of an extract consisting mostly of wax with considerable carotin, but no glyceride. The alcoholic extract postea contained a flavone which was not a quercetin glucoside, it seemed to have a para HO group, and to be similar to quercitagenin of the marigold; there was also a little resin, some saccharose, but no glucose or alkaloid. The aqueous extract had much nitrate, a little caffetannin, and much pectosic mucilage, also an indefinite bitter principle having a para group and turning reddish in air in the presence of lime-water. Further treatment of the leaves indicated a copious deposit of oxalate of calcium, but no reserve starch. The ash amounted to 13.4 per cent of the dried leaf, and contained 41 per cent soluble salts, 4.1 silica, 23.4 CaO, 3.2 MgO, 5.15 P₂O₅, 8.5 SO₃, and 9.6 Cl; there was some manganese, but practically no soluble carbonate. Towards the end of September there is no nitrate in the leaves, but they still have a good deal of tannoid, and a brownish red colouring matter due probably to the oxidation of the amaroid. The flowers are tintured by carotin, and contain a tannoid same as that in the leaves, also have free glucose and a little saccharose. The finely branched, rather shallow, fibrous roots examined on September 30 contained a little caffetannin, a good deal of carbohydrate yielding saccharose and pentose, much pectosic mucilage, but had no starch, nitrate, oxalate, alkaloid, or glucose. The prominent chemical feature of the order Compositæ is the special production of volatile oils, resins, and inulin. Inulin, according to Tanret, is a mixture of two or three substances of high molecular weight, is not reductive, and has no action on beer-yeast or diastase. In the Compositæ it is specially abundant in the colourless regions of the bracts, in the receptacle, rays, corolla, and the developing seeds in all the sub-order Cynarocephalæ. It represents a condensed product of assimilation produced in the shade; i.e., without any special differentiation of the protoplasm, and thus may be regarded as a subordinate stage of that physiological process. A certain definite chemical constitution of the protoplasm may also be concerned in the fact that the corolla rarely produces anthocyan. Of 150 species of Compositæ in the British flora only five produce blue flowers. The quantity of tannin detected is rarely considerable, the process of deassimilation is rarely intense because the plants are richly provided with leaves and bracts, and the flowers although numerous contain only one ovule. Hence the reproductive organs here are readily supplied with all the nitrogen needed without having recourse to the stores thereof contained in the corolla. Yellow flowers, which abound in this order, have a more vigorous anatomical structure than other flowers; i.e., are more completely differentiated and are provided with chromoplastids which make them approach to the character of a true leaf, a sepal, or a bract. "Tubular corollas in Compositæ," says De Candolle, "are yellow, and ligulate corollas are blue, violet, or red; it seems that when they bear stamens their corolla takes the yellow colour of the anthers, and when they are deprived of stamens (ligulate) the corolla assumes the colours of the filaments." However, the economy of nature in these cases seems to be that the corollas of an order of plants which has been described as a "bourgeois wilderness" are made of sterner stuff than those of many other orders. Hence their protoplasm undergoes a specific differentiation which, in addition to starch, fat-oil, and protein-crystals, enables them to form chlorophyll, carotin, and xanthophyll, all of which last need a protoplasmic support without any special solubilisation of albumenoid; i.e., the yellow, orange, and brick-red pigments are products of assimilation only.

Addenda.—In the account of the Water-lily (CHEMICAL NEWS, cxii, 290) the tannoid stated as being present in leaves is myricitrin, and the percentage of P₂O₅ in the ash

of the leaves is 2:13 (not 5:15); the leaves observed on September 12 were a deep purple-red on their upper surface, showing clearly that this foliar coloration is not due to a withdrawal of water, as is sometimes presumed in similar cases; it is undoubtedly due to a withdrawal of nitrogen in the manner and with the results already explained in my previous papers.

Patterdale, Westmorland.

ON THE TRANSFORMATIONS OF PURE IRON.*

By A. E. OXLEY, M.A., D.Sc.,
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THE present communication is composed for the most part of extracts from letters to Sir Robert Hadfield, and deals with the nature of the molecular constitution of pure iron. At Sir Robert's suggestion these extracts are presented to the Faraday Society.

It is now believed by a large school of metallurgists that the A_2 transformation can be satisfactorily explained without assuming allotropic change. The A_3 transformation, on the other hand, is generally regarded as involving allotropy.

But it appears that varied views are taken as to what really constitutes an allotropic change, and until some definite conception of this term is adopted—some criterion which shall decide whether a given transformation does or does not involve allotropy—it seems that no definite advance can be made, for every argument brought forward by one school can always be shown to be inconclusive by another school whose fundamental conceptions are different.

One of the most exacting definitions of allotropy is that given by Benedicks (*Journ. Iron and Steel Inst.*, 1914, lxxxix., 407). The criterion is one of mathematical discontinuity, i.e., two ordinates for the same abscissa. This definition is admirable from a theoretical point of view, but it appears that no experimental work is ever precise enough to approach the demands of such a definition, and therefore it is always open for an opponent to lodge complaints.

A definition which I believe to be satisfactory, and which can also be subjected to direct experimental test, is the following:—

Each different atomic structure of the molecule is an allotropic modification. It is essential, however, to explain the word "different" used here. In some experiments on "The Influence of Molecular Constitution and Temperature on Magnetic Susceptibility" (A. E. Oxley, *Phil. Trans. Roy. Soc.*, 1914, ccxiv., A, 109; and *Ibid.*, 1915, ccv., A, 79), I have frequently been led to the conclusion that the molecules of crystalline, and even of liquid, substances are in a distorted state. This distortion is always very slight and is due to the action of restraining forces exerted by neighbouring molecules on each molecule of the material medium. It is clear, therefore, that the configuration of a molecule in a crystalline medium is slightly different from that of a molecule of the same substance in the liquid. If the mutual influences of the molecule were withdrawn, the molecules of both states would alter their configurations slightly and would become identical. Such a relationship between the molecules is of the nature I have previously called "crystalline grouping," and the distorted condition of the molecule is not to be regarded on the above definition as indicating allotropy. If, indeed, allotropy were determined in this way, then every degree of association would imply a new allotropic form, the number of which forms would be infinite for each substance throughout a finite interval of temperature and "allotropy" would be a useless term.

But if the molecule of the crystalline structure, on

withdrawal of the restraining forces, differ in configuration from a free molecule which has originated in some other way (say by an independent chemical or physical process), either as regards the integral number of atoms in the molecule or the relative distribution of these atoms, even if their number remains the same, then the substance exhibits allotropy. As examples we may take the oxygen to ozone transformation and the many types of isomers known to organic chemistry. Not only has an allotropic modification characteristic physical properties, but, to some extent, characteristic chemical properties too. The constitutional formulæ of modern chemistry are founded on the assumption that the properties of a substance are determined by the nature, number, and mutual dispositions of the atoms within the molecule.

Now the crystalline forms of allotropic modifications will be characteristic, for the space lattice will be conditioned by the configuration of the molecule which determines the restraining forces (*Phil. Trans. Roy. Soc.*, 1915, ccv., A, 79). On the other hand it has been shown (Barlow and Pope, *Trans. Chem. Soc.*, 1906, lxxxix., 1741) that molecules of exactly the same configuration may be packed into quite distinct crystalline aggregates, of different degrees of stability, so that a difference of crystalline symmetry does not necessarily imply allotropy in the sense defined above.

It should be pointed out that this definition is not specially designed to meet magnetic considerations; it is consistent with the recognised chemical view. We must distinguish between the forces holding the molecules in position in the crystalline structure and those holding the atoms together in the molecule (*Ibid.*, loc. cit.), and if the latter forces are large compared with the former (thermochemical evidence that this is so will be given later), then the preservation of molecular identity, and hence the rarity of allotropic change, will not be a surprising phenomenon.

The above remarks lead us to a criterion by which the nature of the so-called β to γ transformation may be discussed. Weiss (*Comptes Rendus*, 1907, cxliv., 25) has shown that the magnetic properties of β and γ iron can be interpreted in terms of a simple atomic constitution of the iron molecule, and the point of importance for us is that the iron molecule consists of two atoms in the temperature intervals of stability of the β and γ forms, and therefore through the transformation from paramagnetic γ iron to ferro-magnetic β iron there is no change in the integral number of atoms constituting the iron molecule. Weiss's work shows that each state of iron provides a measure of the constant of Curie (C), the parameter of the hyperbolæ representing the variation of specific susceptibility as a function of the absolute temperature. In conclusion he states:—

"Le passage du fer β au fer γ qui correspond à la perte des actions magnétique mutuelles sans variation du nombre des atomes de la molécule reste à expliquer, mais la concordance des diverses valeurs de C ne peut être due au hasard."

Hence in so far as the integral number of atoms in the molecule is concerned we cannot regard A_3 as an allotropic change-point.

It is interesting to note that Barlow and Pope (*loc. cit.*, 1741) have pointed out that those elements which crystallise in forms of high symmetry are the ones which show the least tendency to form allotropic modifications. Iron is known to crystallise throughout the β and γ ranges in the cubic system. Further, Reigers (*Zeitschr. Phys. Chem.*, 1894, xiv., 1; the rule holds for 85 per cent of the elements) has shown that the higher the crystalline symmetry of a particular element the smaller, as a rule, is the number of atoms contained in the molecule. These points are consistent, and are in favour of absence of allotropy in iron.

The simple atomic constitution of the iron molecule makes it improbable that changes of physical properties of

* A Paper read before the Faraday Society, October 29, 1915.

iron can be due to a rearrangement of the atoms in the molecule. It is conceivable that the two atoms may be slightly displaced relative to one another as the transformation points are passed, but we cannot regard the resulting iron molecule as a distinct type possessing a new set of properties. Moreover, from a magnetic point of view, assuming that magnetism is to be ascribed to polar molecules, however this polarity may originate, the appearance of ferro magnetism on cooling could not be explained on such a view. Ferro-magnetism demands inter-molecular forces—the forces of crystallisation—although no one doubts that inter-molecular forces and intra-molecular forces are inseparable (*Phil. Trans. Roy. Soc.*, 1915, ccxv., A, 100), and that a small change in the latter may accompany and indeed is essential in a re-grouping of the molecules. If we imagine the inter-molecular restraining forces abstracted, then the molecules of the β and γ forms of iron would be absolutely identical.

If there is no abrupt change of the atomic constitution of the iron molecule, then changes of the properties of pure iron such as occur at A_3 must be ascribed to a change of crystalline grouping of the molecules. This change must be of such a nature that the crystalline symmetry is not affected on passing A_3 ; a change of the closeness of packing of the molecules is all that is required. If the cooling through A_3 is accompanied by a closer grouping of the molecules in the direction (which is characteristic for each crystal) of spontaneous magnetisation, there will be no change of crystalline symmetry, while the increased interaction between the molecules will give rise to spontaneous magnetisation. The variation of molecular distances in the directions perpendicular to that of spontaneous magnetisation for an individual crystal is of small importance from a magnetic point of view, for each molecule is mainly constrained by the molecule in front and the one behind in the direction of its magnetic axis (Ewing, "Magnetic Induction in Iron and Other Metals," 3rd edition, 310). Thus this interpretation is not necessarily inconsistent with known magnetostriction data or with determinations of thermal expansion (linear or volume) of a mass of iron crystals.

If there is a change of molecular arrangement at A_3 , then on passing this point there will be a thermal effect determined by the difference between the internal potential energies above and below A_3 . There may be an accompanying molecular distortion, but this will be slight, and (as pointed out above) cannot be regarded as implying allotropy.

The thermal energy involved on cooling through A_3 is just the heat of transformation from a more open to a closer packed cubic system, as described above, with probably a small contribution from intra-molecular adjustment resulting from the change of packing. As already pointed out, these two parts of the thermal evolution are inseparable, but the existence of the second part does not justify the existence of a new type of iron molecule. Accompanying the re-grouping the iron molecule takes up a slightly distorted appearance of the iron molecule on the other side of A_3 . Under pressure we should no doubt get a slightly different regrouping of the molecules, and, as a consequence, a slight variation of the atomic separation in the molecule. This variation of separation will be different for different pressures, and, therefore, like the phenomenon of association mentioned above, cannot be regarded as implying allotropic change.

It is known that the transformations from ozone to oxygen and from white phosphorus to red are exothermic. The thermal evolutions accompanying allotropic and isomeric changes are comparable with the heats of formation of chemical compounds, and are in general large compared with those involved in the passage from the liquid to the crystalline state or from one crystalline state to another (Pattison Muir, "Elements of Thermal Chemistry," 250). The following are some values of the thermal evolution accompanying known allotropic and isomeric changes:—

Allotropic—

96 grms. ozone = 96 grms. oxygen + 59,200 gr. cal.
31 grms. yellow phosphorus = 31 grms. red phosphorus + 21,000 gr. cal.

Isomeric—

78 grms. dipropargyl = 78 grms. benzene + 100,000 gr. cal.
58 grms. allyl alcohol = 58 grms. acetone + 18,600 gr. cal. = 58 grms. propaldehyde + 22,600 gr. cal.

With these may be compared the following values of the latent heats of fusion of some elements ("Recueil des Constantes Physiques," Paris, 1913, 323):

Element.	Latent heat (gr cals),
Bismuth	13
Cadmium	14
Lead	5
Silver	22
Tin	14
Zinc	28
Gallium	19
Phosphorus	5

These latter values are comparable with the thermal evolution during the transformations of pure iron. From the recalculation curves given by Dr. Arnold ("On a Fourth Recalculation in Steel," 1910, *B.A. Report*, Sheffield) for this substance the rise of temperature is largest for the A_3 transformation point, and is approximately 14° C. Hence, taking the specific heat of iron as 0.1, the thermal evolution at A_3 is 1.4 gr. cal. This small thermal evolution favours the view expressed above that the A_3 transition involves a molecular regrouping, similar to that which occurs in the ordinary process of crystallisation, rather than a rebuilding of the internal structure of the molecule. Therefore from the thermal point of view also, allotropic change, as defined in the present Paper, appears to be absent at A_3 .

The coexistence of thermal expansion and thermal evolution on cooling through A_3 cannot be advanced as an objection to the views developed above, for the same phenomena accompany one another during the transition from water to ice.

I am much indebted to Sir Robert Hadfield, first for suggesting the application of the results of my earlier work to the transformation-points of iron, and second for the encouragement he has given me throughout the whole of our correspondence.

GENERAL DISCUSSION.

Introductory Remarks by the Chairman, Sir ROBERT HADFIELD, F.R.S.

With reference to the very interesting paper now presented by Dr. A. E. Oxley, of the Sheffield University, to whom we are much indebted for the trouble he has taken, it seems to me that he is putting forward theories which well deserve our careful consideration.

Prof. Weiss, of Zurich, has written several valuable papers on the subject of magnetons. Not only is his theory ingenious, but it seems to be suggestive of what is really happening, that is, admitting that the electron and magneton theories themselves, quite apart from their bearing on our particular subject, are eventually found to be correct.

Dr. Oxley appears to have taken up this particular line of thought, and seems to me to have brought this home to our minds in a very clear and practical manner, that is when it is remembered that it is at present purely theoretical; theory, however, often goes before practice.

Without wishing to introduce controversial points, it is, however, necessary to say that Dr. Oxley, at any rate it seems so to me, and others share this feeling, has presented a case which shows that the other critical point of iron, the so-called A_3 point, can also be explained without

calling in the aid of allotropy, thus throwing considerable doubt on allotropy as an explanation for the phenomena met with in the many curious properties of iron alloys, which allotropic explanations have been based almost entirely on the allotropic explanations of the critical points in iron itself.

The allotropic theory has hopelessly broken down, and beta iron has disappeared. As is well known, to explain the curious phenomenon of hardening, this form of iron called "beta" was invoked. It was, however, found that this did not suffice, and another form was raised called "gamma." Even these were insufficient, and it was suggested that there was a fourth form, "delta." In other words, so it seems to me, the theory, interesting and valuable as it has been in invoking discussion and giving rise to research, has broken down. It is admitted that the carbonist point of view has not explained all the difficulties met with, but nevertheless it has gone upon more tangible lines. We know of the existence of carbides, also their properties and characteristics are well known, and they can be isolated. No one has ever seen or handled the so-called allotropic forms of iron. In this direction there could not have been more valuable aid to research than the following papers by Dr. J. O. Arnold, F.R.S. :—

Précis of Various Papers by DR. J. O. ARNOLD, F.R.S.; also DR. A. A. READ.

Researches on the Carbides of Steel.

1. "Chemical Relations of Carbon and Iron." Chemical Society. 1894.
2. "Chemical and Mechanical Relations of Iron, Manganese, and Carbon," Iron and Steel Institute. 1910.
3. "Chemical and Mechanical Relations of Iron, Chromium, and Carbon." Iron and Steel Institute. 1911.
4. "Chemical and Mechanical Relations of Iron, Vanadium, and Carbon." Iron and Steel Institute. 1912.
5. "Chemical and Mechanical Relations of Iron, Tungsten, and Carbon, and of Iron, Nickel, and Carbon." Institution of Mechanical Engineers. 1914.
6. "Chemical and Mechanical Relations of Iron, Cobalt, and Carbon." Institution of Mechanical Engineers. 1915.

It was owing to the importance of this subject, that is the nature and type of different carbides, the writer of these notes offered in this country and on the Continent, also in America, and also to the Metallurgical Division of the Applied Science Department of the Sheffield University, where Dr. Arnold carried on his work, three separate research prizes in the hope that these would stimulate further research in this desirable direction, for surely after the classic work of Abel, Hughes, Arnold, Read, Hogg, Stead, Edwards, Perry, McCance, Carpenter, further aided by Metcalf, Howe, Jullien, T. Sterry Hunt, and Campbell in America, Ledebur, Müller, Osmond, Le Chatelier, Pourcel, Ackerman, and others on the Continent, the rising generation will not rest satisfied until they have torn the veil from one of Nature's most profound and interesting secrets as to why steel containing sufficient carbon turns from a comparatively soft material to one possessing glass-scratching hardness after being heated to certain well-known temperatures and quenched or cooled quickly. The reverse phenomenon is also just as interesting; that is to say, upon taking such a specimen it can be just as quickly restored to its former soft condition by heating and cooling down.

In the same manner, equally interesting and probably concerned with the same problem, are the extraordinary results obtained with certain alloys of iron. For example, manganese steel, which is non-magnetic, can be made magnetic by certain heat treatment described in several of

my papers, while certain alloys of iron with nickel, also iron with nickel and manganese, possess electrical and magnetic qualities of a peculiar nature.

If Dr. Oxley can throw light on these problems by his very excellent and carefully thought-out theory, coming as it does in what may be termed quite a new direction, he will have rendered great service, for underlying theoretical consideration are the important facts of practical application. Whilst it is true the correct understanding of the heat treatment of steel controlling and varying the temperatures to which it is heated to obtain certain desired physical properties has advanced with marvellous rapidity during the last ten years, thanks very largely to such men as Osmond, H. Le Chatelier, Arnold, Roberts-Austen, Callendar, Howe, Stead, Burgess, and others, there is still much to be learned, still much unexplained, in the many curious problems met with.

I will not here discuss Dr. Oxley's theories, that is for those present at the meeting; but I would like to say that it would appear to be in some new direction, such as that set forth by Dr. Oxley, where we shall have to look for advancing our knowledge. Thus this discussion may be the starting-point of quite a new line of thought, which, whilst it will leave the allotropist and the carbonist each to go on his own way and continue his useful researches, may not Dr. Oxley's paper eventually bring them together and a common and correct explanation be found.

RADIOMETRIC MEASUREMENTS OF THE IONISATION CONSTANTS OF INDICATORS.*

By E. J. SCHAEFFER, M. G. PAULUS, and HARRY C. JONES.

(Continued from p. 198).

The Spectroscope.—The grating spectroscope was designed and built in the Physical Laboratory under the direction of Prof. John A. Anderson. The use of such a spectroscope presents two especially desirable advantages—first, the position of regions of absorption can be very accurately determined; second, due to its high resolving power, the structure of even the very narrow absorption bands and some absorption lines can be studied in detail. The spectroscope is so constructed that either the photographic plate or any of the radiometric instruments can be used with it. The use of the radio-micrometer enables us to determine not only the actual positions of regions of absorption, but also to make quantitative measurements of the light transmitted by a solution for a wide range of wave lengths. The deflections of the radio-micrometer give an accurate measure of the relative intensities of the different absorption bands and of the different parts of the same bands. It will thus be seen that the radiometric method has distinct advantages over the photographic method, which is chiefly useful in determining the positions of regions of absorption and the general characteristics of the visible spectrum as transmitted by the solutions. Moreover, the photographic plate is only sensitive from $\lambda = 0.2 \mu$ to $\lambda = 0.76 \mu$, whereas with the radio-micrometer and the apparatus used in this work quantitative measurements of absorption could be made from $\lambda = 0.4 \mu$ to $\lambda = 2.0 \mu$, using slits only 1 mm. in width. Considering the high dispersion that could be obtained with the four-inch grating, this width of slit gives a very pure spectrum.

The plane four-inch grating with which the spectroscope is equipped was ruled by Anderson, and the ruling is of such a character that a very bright first-order spectrum is produced. This is quite essential for radiometric measurements in the visible region of the spectrum. Energy measurements were made in both first-order spectra, one

* This investigation was carried out with the aid of a grant from the Carnegie Institution of Washington generously awarded to H. C. Jones. From *Journal of the American Chemical Society*, xxxvii., No. 4.

being on each side of the central image. The spectrum on one side was found to be somewhat more intense, and therefore this brighter side was used.

If either the intensity of the light source or the sensitivity of the radio-micrometer exceeds certain limits it is possible that light energy from the second-order spectrum will vitiate the energy measurements made in the first-order spectrum. This will be readily seen if we consider that wave length of light $\lambda = 0.35 \mu$ of the second order overlaps wave length of light $\lambda = 0.7 \mu$ of the first order, &c. Therefore it was desired to know if, with a Nernst glower burning at 0.8 ampère and 120 volts, the second-order spectrum had sufficient energy to be detected by the radio-micrometer. If such proved to be the case it would be found necessary to introduce colour screens to eliminate the light energy from the second-order spectrum. That the first-order spectrum can be regarded as pure is shown by the following considerations:—

Glass cuts off all wave lengths of light beyond $\lambda = 0.35 \mu$. Since the glass in the path of the light is of considerable thickness the first-order spectrum is not contaminated with any light from the second-order spectrum as far out as $\lambda = 0.7 \mu$ of the first order. A solution of copper sulphate is entirely transparent to all wave lengths of light shorter than $\lambda = 0.6 \mu$. A 10 mm. depth of a saturated solution of copper sulphate shows complete absorption beyond $\lambda = 0.6 \mu$. Using the above solution of copper sulphate, radiometric measurements were made from $\lambda = 0.4 \mu$ to $\lambda = 1.3 \mu$. Beyond $\lambda = 0.6 \mu$ the solution of copper sulphate is entirely opaque, and therefore no evidence of light energy from the second order was obtained as far out as $\lambda = 1.3 \mu$. It has already been shown that the first-order spectrum is pure up to $\lambda = 0.7 \mu$, and the above shows that the light from the overlapping second order spectrum does not contain a sufficient amount of energy to be detected by the radio-micrometer as far out in the infra-red as $\lambda = 1.2 \mu$ of the first-order spectrum. The radiometric measurements of the dissociation constants of the indicators were all made between $\lambda = 0.5 \mu$ and $\lambda = 0.6 \mu$, and in this region the first-order spectrum is absolutely pure.

The drum head which rotated the grating through definite angles is a large one, its diameter being four inches. It is attached to a very carefully constructed screw, so designed that each complete revolution changes the wave length of light falling on the slit by approximately 500 Angstrom units. The drum contains 500 divisions, and, all things considered, it is quite probable that the wave length settings are accurate to within one or two Angstrom units.

The spectroscope is of the Littrow mounting, the same lens serving both as telescope and collimator. It is provided with two four-inch lenses made by Brashear. One lens has a focal length of 72 inches and is intended for photographic work; the other, and the one which was used in this work, has a focal length of 30 inches. With this lens, the visible first-order spectrum at slit s_2 has a length of over six inches. Provision has also been made for the mounting of a large glass prism on the grating table, and it is purposed to use this prism when an intense first order spectrum is desired rather than a spectrum which is widely dispersed. Had we not been successful in constructing a very sensitive radio-micrometer it would have been necessary to make frequent use of the glass prism.

The spectroscope was placed in a brass box, blackened on the inside, which prevented stray sources of light from reaching the grating. The slits were of the bilateral type.

The calibration curve for the grating and drum head was calculated from the known grating space by means of the equation—

$$\lambda = 33866.7 \sin \frac{3000T + 6R}{3500}$$

where T is the number of complete turns of the screw which rotates the grating and R is the reading on the drum. The calibration was also effected by observing the posi-

tions of various mercury, sodium, and lithium lines. It was decided that the calculated values are more accurate than the observed, and accordingly the dispersion curve based on the calculated values was used.

Source of Light.—A Nernst glower served as the source of light, the electrical energy being supplied by a series of storage batteries. By means of a rheostat the light intensity could be kept quite uniform. The glower was protected from air draughts by means of a box of asbestos wood. Provision was also made for the mounting of a nitrogen lamp when it was desired to secure large deflections of the radio-micrometer for wave lengths of light shorter than $\lambda = 0.5 \mu$. (Dr. W. R. Whitney, of the General Electric Company, very kindly supplied us with two lamps of special design to be used for this purpose).

The Cells.—A very important part of the equipment is the cells which contain the solutions to be investigated. There are two cells, both made as nearly alike as possible. The cell consists of two brass cylinders, which closely telescope into one another. One end of each cylinder is closed by a glass plate, held in position by Wood's fusible metal. The four glass ends used in the cells are all of the same thickness—i.e., 2 mm. Their surfaces are plane, and are parallel to within five wave lengths of light. It is a difficult problem to set these plates in the brass cylinder with Wood's fusible metal without warping them and destroying their plane-parallelism. The character of the interference fringes which the plates gave with the mercury arc determined when they were correctly adjusted. A fine thread was "chased" on the outer cylinder. This thread carried a nut, which when turned raised or lowered the inner cylinder a definite amount. Each complete revolution of this nut changed the distance between the plates by 1 mm. The nut contained 100 divisions, and by means of this arrangement we could readily adjust the depth of the solutions to within less than 0.01 mm. Each cell was then filled with a layer of water 5 mm. in depth, and the deflections given by the radio-micrometer were noted for a light source of uniform intensity throughout the whole region of the spectrum under investigation, namely, from $\lambda = 0.4 \mu$ to $\lambda = 2.0 \mu$. The deflections should agree with each other very closely for all wave lengths of light if the cells are optically identical. Having made sure that the cells are optically identical, they were heavily plated with gold, to remove any possibility of the solutions attacking the metals of the cell. It is very important to keep the solutions perfectly clear when measurements are being made, and the glass ends must be maintained absolutely clean. Table I. shows the optical identity of the two cells. Under Cell A and Cell B are given the actual radio micrometer deflections for various wave lengths of light.

TABLE I.

$\lambda = A. U.$	Cell A.	Cell B.	$\lambda = A. U.$	Cell A.	Cell B.
4546	4'0	4'0	8029	125'0	125'0
4797	8'2	8'2	8275	127'0	127'5
5047	14'2	14'5	8520	129'0	129'0
5298	22'0	22'5	9009	129'5	130'0
5548	31'5	31'5	9497	115'5	115'0
5797	41'5	41'7	9982	105'5	106'0
6046	50'5	50'5	10465	113'5	114'0
6295	60'7	60'5	10946	108'5	108'0
6543	70'5	71'2	11424	69'0	69'0
6792	86'7	86'5	11900	51'5	52'0
7041	100'5	100'0	12373	56'0	56'0
7290	107'7	107'7	12843	53'5	54'0
7536	114'0	114'5	13314	34'0	34'0
7784	120'5	120'5	13775	11'0	10'7

Having discussed the principal parts of the apparatus, viz., the radio-micrometer, spectroscope, source of light, and the cells, and having shown how they meet the requirements demanded by work of this character, it is desirable to consider next the general arrangement of the various parts.

Arrangement of Apparatus.—The Nernst glower, lenses, prisms, and carriage for the cells were mounted on an upright steel standard placed by the side and near the end of the spectroscope, next to the radio-micrometer. Parallel light from the Nernst glower was made to pass, by means of a carefully adjusted sliding carriage, first through one cell and then through the other. The two cells could thus be made to occupy the same position in the path of the light. The light transmitted by the solutions contained in the cells was then deflected by means of a right-angle prism and focussed on the slit of the spectroscope s_1 . Inside of the box inclosing the spectroscope and directly in the rear of slit s_1 was placed another right-angle prism, which reflected the light through a four-inch lens to the grating. The dispersed light was reflected back through this same lens and focussed on the slit of the spectroscope s_2 . The light which emerged through slit s_2 was again brought to a focus on the junction of the radio-micrometer. By turning the drum head of the spectroscope to the proper points we could then determine quantitatively the light transmitted by any solution for all wave lengths of light between $\lambda = 0.4 \mu$ and $\lambda = 2.0 \mu$.

The Differential Method.—It was desired to measure the absolute percentage transmission of 20 mm. of solution. This was done by a differential method which eliminated corrections for reflection from the glass ends, and differences in the refractive index of the glass and the solutions. The method of procedure is as follows:—Cell A is filled with 21 mm. of solution, cell B with 1 mm. of solution. Light of unvarying intensity I_0 was then passed through cell A, and the intensity of the transmitted light I_1 measured by means of the radio-micrometer. As soon as possible cell B was made to occupy the same position formerly occupied by cell A, and the intensity of its transmitted light I_{11} determined. The deflection produced when cell A was in the path of light, divided by that given when cell B occupied the same position, determines the absolute percentage transmission for 20 mm. of solution, or in other words, I_1 / I_{11} is the value desired. The justification for this procedure is seen from what follows:—

If the depth of solution under investigation is l , the intensity of the incident light I_0 , and that of the transmitted light I , we have the following relations for depths of solution l' and l'' :—

$$I_1 = I_0 e^{-kl'} \quad (a)$$

$$I_{11} = I_0 e^{-kl''} \quad (b)$$

Dividing a by b we get—

$$I_1 / I_{11} = e^{k(l'' - l')} \quad (c)$$

But the actual percentage transmission of the same solution of depth $l' - l'' = l$ is given by—

$$I / I_0 = e^{-k(l' - l'')} = e^{-k(l'' - l')}, \text{ or } I_1 / I_{11} = I / I_0. \quad (d)$$

(To be continued).

British Association Committee on Fuel Economy.
—As an outcome of the recent Manchester Meeting, the British Association has invited the following gentlemen to serve on a Committee to consider and report upon the question of Fuel Economy (Utilisation of Coal and Smoke Prevention), from a national point of view:—Prof. W. A. Bone, F.R.S., of the Imperial College of Science and Technology, London (Chairman); Mr. E. D. Simon, Chairman of the Manchester Air Pollution Committee (Secretary); Profs. P. P. Bedson (Armstrong College, Newcastle-on-Tyne); J. W. Cobb and J. B. Cohen, F.R.S. (Leeds University); H. B. Dixon, F.R.S. (Manchester University); Thomas Gray (Royal Technical College, Glasgow); H. S. Hele Shaw, F.R.S. (London); L. T. O'Shea and W. P. Wynne, F.R.S. (Sheffield University); and Richard Threlfall, F.R.S. (Birmingham); together with Dr. G. T. Beilby, F.R.S. (Glasgow); Mr. Ernest Bury and Dr. J. E. Stead, F.R.S. (Middlesbrough and the Cleveland District). The Committee, which is empowered to add if necessary to its members, has been selected so as to include representative chemists, engineers, and technologists from all the principal industrial areas.

STUDIES IN THE STEREOCHEMISTRY OF QUINQUEVALENT NITROGEN.*

RESOLUTION OF THE ASYMMETRIC QUATERNARY AMMONIUM COMPOUNDS.

By SHIGERU KOMATSU.

THE author has already shown in his previous article (*Mem. Coll. Sci. Eng., Kyoto*, 1912, iii., 371), that the four negative valencies of the nitrogen atom in the quaternary ammonium compounds are of the same value, but it has still remained as a question that the melting-point of compound formed by one and the same method is different in the statements of different investigators.

Hence, the present work was undertaken to decide whether the author's substance is a true asymmetric compound or not, and at the same time to study the spatial configuration of atoms or atomic groups in the molecule.

Pure methyl *n*-propyl phenyl benzyl ammonium iodide prepared from methyl *n*-propyl aniline and benzyl iodide, was mixed with equi-molecular quantity of anhydrous silver salt of dextro-bromocamphorsulphonic acid in an acetone ethyl acetate solution, and boiled on a water-bath for two hours. The filtrate separated from silver iodide was subjected to distillation to remove the solvent, and the yellow syrupy residue changed to a solid mass on allowing to stand in a desiccator over a night. The crystalline mass consisting of a mixture of dextro and laevo methyl *n*-propyl phenyl benzyl ammonium dextro-bromocamphorsulphonate, was dissolved in hot acetone and left in a desiccator.

The crystals melting at $161-162^\circ$ gave a specific rotatory power $[\alpha]_D^{25} = +51.68^\circ$ in an aqueous solution, which corresponds to that of the racemic ammonium dextro-bromocamphorsulphonate.

Then, the whole mass was dissolved in ethyl acetate, and from such a solution laevo methyl *n*-propyl phenyl benzyl ammonium dextro-bromocamphorsulphonate isolated in white needle-shaped crystals. The mother-liquor was made to evaporate down to a small bulk, and some ether added in order to promote the further crystallisation. Adding more ether to the filtrate from the second crop of the crystals, we have obtained hygroscopic needle-shaped crystals, and finally a syrupy residue containing dextro methyl *n*-propyl phenyl benzyl ammonium dextro-bromocamphorsulphonate. To the syrup dissolved in water was added a potassium iodide solution in order to precipitate all the sulphonate present as the crystalline iodide, and methyl *n*-propyl phenyl benzyl ammonium iodide thus formed was allowed to re-crystallise from alcohol.

It melts at 148° , and its specific rotatory power in its alcoholic solution was found to be $[\alpha]_D^{25} = +90.90^\circ$.

The three fractions of the active bromocamphorsulphonate crystallised out from the ethyl acetate regularly increase their hygroscopic character from the first to the third, also showing the difference in the specific rotatory power in their aqueous solutions, i.e., $[\alpha]_D^{25} = +1.48^\circ$, $[\alpha]_D^{25} = -0.87^\circ$, and $[\alpha]_D^{25} = -2.57^\circ$ respectively.

Repeating the re-crystallisation of the first fraction several times from ethyl acetate, finally it was found to possess the constant rotatory power $[\alpha]_D^{25} = -2.57^\circ$, which agrees with that of the pure laevo methyl *n*-propyl phenyl benzyl ammonium dextro-bromocamphorsulphonate. The substance thus obtained was no longer hygroscopic as was observed by Jones (*Journ. Chem. Soc.*, 1906, lxxxix., 281), and has no definite melting-point. Colourless crystals when heated at 80° for a while became opaque, and the cause of such a phenomenon is due to the escape of the ethyl acetate of crystallisation which is contained in the molecule, as was ascertained by the author by the usual method.

The melting-points and rotatory powers in the alcoholic solutions of the active ammonium iodide, bromide, and

* *Memoirs of the College of Science, Kyoto Imperial University*, 1915, i, No. 3.

chloroplatinate derived from optically active ammonium dextro-bromocamphorsulphonates, have been studied, and the results of the experiments by the author together with those of Wedekind and Fröhlich ("Zur Stereochemie d. fünfwertigen Stickstoffes," 1907, S. 49), are shown in the Table I.

TABLE I.

Wedekind and Fröhlich.	Author.
$l\text{-(CH}_3\text{)(C}_3\text{H}_7\text{)(C}_6\text{H}_5\text{)(C}_7\text{H}_7\text{)N.C}_{10}\text{H}_{13}\text{BrSO}_4\text{—}$	
$[\alpha]_{\text{D}}^{25} = -2.67^\circ$	$[\alpha]_{\text{D}}^{25} = -2.57^\circ$
$l\text{-(CH}_3\text{)(C}_3\text{H}_7\text{)(C}_6\text{H}_5\text{)(C}_7\text{H}_7\text{)NI—}$	
$\{ \begin{array}{l} [149-150^\circ] : \\ [\alpha]_{\text{D}}^{25} = -96.47 \end{array} \}$	$\{ \begin{array}{l} [146-147^\circ] ; \\ [\alpha]_{\text{D}}^{25} = -93.63^\circ \end{array} \}$
$l\text{-(CH}_3\text{)(C}_3\text{H}_7\text{)(C}_6\text{H}_5\text{)(C}_7\text{H}_7\text{)NBr—}$	
$\{ \begin{array}{l} — \\ — \end{array} \}$	$\{ \begin{array}{l} [166-167^\circ] ; \\ [\alpha]_{\text{D}}^{25} = -124.3^\circ \end{array} \}$
$l\text{-[(CH}_3\text{)(C}_3\text{H}_7\text{)(C}_6\text{H}_5\text{)(C}_7\text{H}_7\text{)NCl}]_2\text{PtCl}_4\text{—}$	
$\{ \begin{array}{l} — \\ — \end{array} \}$	$\{ \begin{array}{l} [163.5-164^\circ] \\ [\alpha]_{\text{D}}^{25} = +90.90^\circ \end{array} \}$
$d\text{-(CH}_3\text{)(C}_3\text{H}_7\text{)(C}_6\text{H}_5\text{)(C}_7\text{H}_7\text{)NI—}$	
$[\alpha]_{\text{D}}^{25} = +86.74^\circ$	

The author has attempted to resolve α -methyl allyl phenyl benzyl ammonium iodide prepared from methyl benzyl aniline and allyl iodide, into its optical antipodes by means of silver dextro-bromocamphorsulphonate in an acetone or ethyl acetate solution, and the white platy crystals obtained by the fractional crystallisation of the racemic methyl allyl phenyl benzyl ammonium dextro-bromocamphorsulphonate in the acetone solution, melted at $135-136^\circ$, and gave the specific rotatory power, $[\alpha]_{\text{D}}^{25} = +51.59^\circ$, in an aqueous solution. After a repeated crystallisation from acetone the rotatory power of the substance was again determined, and observed to be $[\alpha]_{\text{D}}^{25} = +52.28^\circ$, and γ -methyl allyl phenyl benzyl ammonium dextro-bromocamphorsulphonate like the α -compound, also melted at $135-136^\circ$ and gave the specific rotatory power, $[\alpha]_{\text{D}}^{25} = +52.77^\circ$.

Thus the author's endeavour to resolve methyl allyl phenyl benzyl ammonium iodides (both α - and γ -forms) by means of bromocamphorsulphonic acid, into optically active compounds has not been successful.

The author therefore used Pope and Peachey's method (*Journ. Chem. Soc.*, 1899, lxxv., 1127; 1901, lxxix., 828), and fortunately succeeded in resolving both ammonium iodides into their optically active forms.

Pure α -methyl allyl phenyl benzyl ammonium iodide and anhydrous silver dextro-camphorsulphonate mixed in equimolecular quantities in an acetone ethyl acetate solution was heated over a water-bath for one and a-half hours. After separating silver iodide the solution was subjected to distillation, and the residue consisting of a viscid liquid, when allowed to stand over sulphuric acid in a dark and cold place for a week, deposited crystals. By repeating fractional crystallisation from acetone six times there were obtained white needle shaped crystals melting at $161-162^\circ$, which gave the mean specific rotatory power of $[\alpha]_{\text{D}}^{25} = +46.48$ in an aqueous solution. From the mother-liquor crude *laevo* α -methyl allyl phenyl benzyl ammonium iodide was isolated by the aid of a potassium iodide solution, which was utilised for the preparation of the pure *laevo* isomeride.

In the winter time when the author repeated the same experiment the yield of the crystalline mass consisting of a mixture of dextro and *laevo* methyl allyl phenyl benzyl ammonium dextro-camphorsulphonates was more fruitful, owing to the influence of the external conditions—temperature and humidity of the atmosphere. In the fractional crystallisation of the racemic camphorsulphonates ethyl acetate was used as a solvent according to Pope and Harvey (*loc. cit.*).

The first crop of the crystals consisted of almost pure dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate, which when re-crystallised from ethyl acetate five times, and then from acetone twice, formed

white needle-shaped crystals melting at $162-163^\circ$, whose specific rotatory power in an aqueous solution was found to be $[\alpha]_{\text{D}}^{25} = +46.71^\circ$ as the mean value. The second crop consisted of white needle-shaped crystals, and the third hygroscopic rhombic crystals, and their rotatory powers, determined in aqueous solutions, were observed to be $[\alpha]_{\text{D}}^{25} = +38.27^\circ$ and $[\alpha]_{\text{D}}^{25} = -1.28$ respectively.

The crude *laevo* ammonium iodide separated from the mother-liquor from the last crop was treated with an equimolecular silver *laevo*-camphorsulphonate. Carrying out the process of the crystallisation of the reaction product as described in its optical antipode, pure *laevo*-methyl allyl phenyl benzyl ammonium *laevo*-camphorsulphonate was obtained in white needle-shaped crystals melting at $160-161^\circ$, which in an aqueous solution gave the mean specific rotatory power of $[\alpha]_{\text{D}}^{25} = -46.49$.

(To be continued).

MISCELLANEOUS.

Recent and Forthcoming Books.—The list issued by Messrs. Charles Griffin and Co., Ltd., contains some highly interesting items, and important treatises are included among the War-Help Books for manufacturers and students. A fifth revised edition of Harbord and Hall's "Metallurgy of Steel" has been issued, and other books on steel are that of Sir Robert Hadfield on "Researches on Special Steels," and of Prof. Edwards on "The Physico-Chemical Properties of Steel." A fourth edition of Prof. Turner's "Metallurgy of Iron" has also been prepared. For students of aeronautics there is a fully illustrated concise study of "The Aeroplane," by A. Fage, A.R.C.S., and "Aero Engines," by G. A. Burls, M.Inst.C.E. Among books intended for industrial purposes may be mentioned a text-book on the "Analysis of Dye-stuffs," by Prof. A. E. Green, which has already been noticed in the CHEMICAL NEWS, a "Manual of Oils, Resins, and Paints," by Ingle and Sutcliffe, and "The Manufacture of Ink," by Mitchell and Hepworth. These titles by no means exhaust the list, which includes also some of the latest and most up-to-date works on Mining, Surveying, General Metallurgy, &c.

Specific Reaction of Picric Acid.—G. Rodillon.—Very small quantities of trinitrophenol can be characterised as follows:—To some cc. of the liquid supposed to contain picric acid about one quarter of pure HCl is added, and then some fragments of zinc. The nascent hydrogen evolved brings about reduction, and the yellow colour of the nitrophenol disappears. After a little while when the reduction appears to be complete, the liquid is decanted from the zinc into another tube, and some drops of hydrogen peroxide are added and mixed by shaking. Then a layer about 2 cm. high of pure ammonia is added without shaking. If the original liquid contains picric acid at the zone of contact of the two liquids two adjacent coloured rings are formed; in the upper alkaline liquid a blue violet and in the lower acid liquid a reddish violet ring. If the liquid is then shaken, as long as it remains acid, it all turns blue violet, resembling the coloration given by methylene blue. The blue violet ring of the ammoniacal layer is specific of the presence of picric acid. To apply this test to foods or objects coloured with picric acid they are broken up and extracted with warm water till about 250 cc. of liquid is obtained, which is then treated as described below. For urine or beer 250 cc. of the liquid are made strongly acid with pure hydrochloric acid, extracted with 50 cc. of benzine or ether, shaken up, and then decanted. This process is repeated three times, and then the volatile liquids thus decanted off are put together and evaporated to dryness. The residue is then taken up with a few cc. of water, and treated as described at first.—*Journal de Pharmacie et de Chimie*, 1915, xii, No. 6.

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ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION. MANCHESTER, 1915.

By Prof. W. A. BONE, D.Sc., F.R.S., President of the Section.

Gaseous Combustion.

THIS year is, as many of you are doubtless aware, the centenary of Davy's invention of the miner's safety lamp, which formed the starting-point of his brilliant researches upon flame, in which he disclosed, and brought within the range of experimental inquiry, most of the intricate and baffling problems connected with the fascinating subject of gaseous combustion. Also the ground on which we meet to-day is known to the whole scientific world as the place where, during more than a quarter of a century of continuous investigation, a succession of Manchester chemists, led and inspired by Prof. H. B. Dixon, have devoted themselves to the elucidation of the many problems which Davy's work foreshadowed. Therefore, both in point of time and place, the occasion is singularly appropriate for a review of recent advances in this important field of scientific inquiry.

At the Sniffield meeting of the Association in 1910, I had the honour of presenting to a joint conference of Sections A and B (Physics and Chemistry) a report summarising the then "State of Science in Gaseous Combustion" (*Journal of Gas Lighting*, cxi., 648), which gave rise to a keen and stimulating discussion, and was not only printed *in extenso* in the Annual Reports for that year, but was also widely circulated through the medium of the Scientific and Technical Press. There is no need therefore for me to refer in any detail to the results of researches already dealt with in that report. I can more usefully devote part of the time at my disposal to supplementing it with a review of more recent researches, which have considerably extended our knowledge in many directions.

Ignition Phenomena.

The first section of my 1910 report was concerned with ignition temperatures and the initial phases of gaseous explosions, and it is in connection with ignition phenomena that subsequent progress has been most marked.

For the ignition of a given explosive mixture, it is necessary that the temperature of its constituents should be raised, at least locally, to a degree at which a mass of gas self-heats itself by combination until it bursts into flame, or, in other words, to a degree at which the chemical action becomes autogenous or self-propelling, so that it quickly spreads throughout the whole mass. This particular degree, or in some cases range, of temperature is commonly spoken of as the ignition-point of the mixture; but in using the expression, certain qualifications should be carefully borne in mind. In the first place, as H. B. Dixon and H. F. Coward showed in 1909 (*Ibid.*, cvii., 323), whereas when certain combustible gases—such, for example, as hydrogen and carbon monoxide, the mechanism of whose combustion is probably of a fairly simple character—and air or oxygen are separately heated in a suitable enclosure before being allowed to mix, the temperature at which ignition occurs lies within a very narrow range, which is, within the limits of experimental error, the same for both air and oxygen (*i.e.*, in the case of hydrogen it is 530° to 590° , and for carbon monoxide 640° to 658°). On the other hand, in cases where the mechanism of combustion is known to be very

complex (*i.e.*, hydrocarbons), the ignition range is either fairly wide or else is materially lower in oxygen than in air (or both). Thus—

	In air.	In oxygen
Methane	650° — 750°	556° — 700°

The explanation of such behaviour is probably to be sought in the known complexity of the combustion, and the marked tendency for appreciable and fairly rapid interaction between the inflammable gas and oxygen before the actual ignition-point is reached. If, by any means, such preliminary interaction could either be entirely suppressed, or if, on the other hand, it be very rapid in character, the observed "ignition range" would be narrowed, as is actually the case with ethylene (542° to 547° in air, and 500° to 519° in oxygen).

There are two other means by which an explosive mixture may be ignited. One is by adiabatic compression, and the other, and most commonly employed of all, is by the passage of an electric spark. The adiabatic compression of an explosive mixture was originally suggested by *Nernst* as a means of determining its ignition-point, provided (1) that ignition is not produced locally, while the main temperature of the gas is still far below the true ignition temperature, (2) that the piston of the apparatus does not move appreciably after the gas has been raised to its ignition-point. At the time of my 1910 report, *Falk*, in America, had applied the method in the case of hydrogen and oxygen mixtures, with results which, in the light of more recent work, would appear to have been misleading or erroneously interpreted. Thus, for instance, he found that of all the mixtures of hydrogen and oxygen, the equimolecular $H_2 + O_2$ mixture has the lowest ignition temperature (514°), from which he concluded that the gases react initially to produce hydrogen peroxide rather than steam. Such a conclusion, which I believe to be erroneous, naturally directed attention to the experimental method involved.

The subject was promptly taken up here, in Manchester, by H. B. Dixon and his co-workers, with the result that much new light has been thrown on the phenomena accompanying ignition (H. B. Dixon, L. Bradshaw, and C. Campbell, *Trans. Chem. Soc.*, 1914, cv., 2027; H. B. Dixon and J. M. Crofts, *Ibid.*, p. 2036). The ratio of the ignition temperature to the initial temperature of the mixture before compression, both expressed in degrees absolute, $\left(\frac{T_2}{T_1}\right)$, may be calculated from the compression ratio, $\left(\frac{V_1}{V_2}\right)$, by means of the well-known formula for adiabatic compression:—

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1};$$

where γ = the ratio of the specific heats at constant pressure and volume, respectively, of the mixture compressed, and which for a mixture of diatomic gases, such as hydrogen and oxygen, is usually taken as 1.40.

Dixon's recent photographic analysis of the appearance of flame when mixtures of carbon bisulphide and oxygen, $CS_2 + 3O_2$, are adiabatically compressed, have proved that the flame, starting from a point or layer, always takes an appreciable time to spread through the mixture, and that unless special precautions are taken to arrest the piston at the moment of its attainment of the ignition condition, it may be driven in much further than the minimum distance for ignition. The real ignition-point, as above defined, is not necessarily synchronous with the actual appearance of the flame. There may be, and usually is, an appreciable "pre-flame" period. Only in the fastest-burning mixtures is this period negligible; hence the necessity of artificially stopping the movement of the piston at the beginning of the period—a precaution which *Falk* seems to have neglected.

According to Dixon and Crofts' recent determination by this method of the ignition-points of mixtures con-

taining electrolytic gas, whereas successive additions of hydrogen or nitrogen progressively raise the ignition temperature of the undiluted gas by regular increments, as would be supposed, successive additions of oxygen, on the other hand, lower it, as a glance at Table I. will show.

TABLE I. Ignition-points of Mixtures containing Electrolytic Gas by Adiabatic Compression.

(H. B. DIXON and J. M. CROFTS, 1914).

Electrolytic gas, $2\text{H}_2 + \text{O}_2 = 526^\circ$.

$+ x\text{H}_2$	$+ x\text{N}_2$	$+ x\text{O}_2$
$x = 1 \quad 544^\circ$	$x = 1 \quad 537^\circ$	$x = 1 \quad 511^\circ$
$x = 2 \quad 561^\circ$	$x = 2 \quad 549^\circ$	$x = 7 \quad 478^\circ$
$x = 4 \quad 602^\circ$	$x = 4 \quad 571^\circ$	$x = 15 \quad 472^\circ$
$x = 8 \quad 676^\circ$	$x = 8 \quad 615^\circ$	
$(526 + 18 x)^\circ$	$(526 + 11 x)^\circ$	

The observed raising effects of successive dilutions with hydrogen and nitrogen call for no comment, save that the relatively greater effect of hydrogen as compared with nitrogen may be attributed to its greater thermal conductivity; but the lowering effect of oxygen is indeed puzzling, and its meaning can only be conjectured. Dixon and Crofts have suggested that it may be due either to the formation of some active polymeride of oxygen under the experimental conditions, which seems to me doubtful, or that the concentration of oxygen in some way or other brings about increased ionisation of the combustible gas. This at once raises the larger question of whether or not ignition is a purely thermal problem, as until recently has generally been supposed.

Prof. W. M. Thornton, of Newcastle-upon-Tyne, recently published some very suggestive work on the "Electrical Ignition of Gaseous Mixtures" (*Proc. Roy. Soc.*, 1914, A, xc., 272; xc., 17), which, apart from its theoretical interest, has an important bearing on the safety of coal-mines where electrical currents are used for signalling and other purposes.

The common belief that any visible spark will ignite a given explosive mixture of gas and air is, of course, quite erroneous; for just as Coward and his co-workers have shown that for a given explosive mixture and sparking arrangement there is a certain limiting pressure of the gaseous mixture below which ignition will not take place, so from Thornton's work it would appear that a definite minimum of circuit energy is required before a given mixture at given pressure can be ignited by a spark. And, moreover, he has stated that the circuit energy required for the spark ignition of a given mixture, say, of methane and air is something like 56 times greater with alternating than with continuous current at the same voltage. From this he has argued that the igniting effect cannot be simply thermal, but must be in part at least ionic. This conclusion he further supports with the statement that the igniting power of a unidirectional current is proportional to the current in the case of many gaseous mixtures over an important part of their working range of inflammability.

While there is much that is suggestive in Thornton's work, there is also a good deal which seems very difficult to interpret from a chemical standpoint. I here refer more particularly to his later supposition of "stepped ignition," which is based upon certain observed abrupt increases in the minimum igniting current required with condenser discharge sparks as the proportion of combustible gas in the air mixture examined progressively increases. In other words, it is claimed that continuous alteration of the proportions of gas and air in an explosive mixture is, or may be, accompanied by discontinuous alterations in the spark energy required for ignition. I must confess that, after careful examination of the published curves, I am quite at a loss to give them any chemical interpretation, and to being somewhat sceptical about the supposed "stepped ignition." A repetition and extension of Prof. Thornton's experiments would be most valuable as a means to a better understanding of the conditions of spark ignition.

Influence of Electrons upon Combustion.

During the discussion upon my 1910 report, Sir J. J. Thomson reminded us chemists that combustion is concerned, not only with atoms and molecules, but also with electrons moving with very high velocities. They might be a fact of prime importance in such intensive forms of gaseous combustion as are realised in contact with hot or incandescent surfaces, as also in the explosion wave. It is well known, of course, that incandescent surfaces emit enormous streams of electrons travelling with high velocities, and the actions of such surfaces may be due to the formation of layers of electrified gas in which chemical changes proceed with extraordinarily high velocities. Again, the rapidity of combustion in the explosion wave might, he thought, conceivably be due to the molecules in the act of combining sending out electrons with exceedingly high velocities, which precede the explosion wave and prepare the way for it by ionising the gas.

With regard to this interpretation of the action of surfaces, Mr. Harold Hartley carried out a promising series of experiments in my laboratory at Leeds University upon the combination of hydrogen and oxygen in contact with a gold surface which lend some support to the idea. But they require further extension before it can be considered as finally proved. It is my intention in the near future to resume the systematic investigation of the matter as rapidly as circumstances permit; but the experimental difficulties are formidable, and the mere chemist working by himself may easily be misled. We badly need the active co-operation of physicists in elucidating the supposed rôle of electrons in combustion.

Prof. H. B. Dixon and his pupils have, at Sir J. J. Thomson's suggestion, recently tested the idea as applied to the explosion wave, with, however, negative results (*Proc. Roy. Soc.*, 1914, A, xc., 506). It is known, of course, that the motion of the ions can be stopped at once by means of a transverse magnetic field, in which they curl up, and are caused to revolve in small circles, and the question which Prof. Dixon decided to put to the test of experiment was whether the damping of the electronic velocities in a powerful magnetic field would have any appreciable effect either upon the initial phase of an explosion or upon the high velocity of detonation. But though he employed a very intense magnetic field produced by some powerful magnets specially constructed by Sir Ernest Rutherford for the deflection of electrons of high velocity, no appreciable effect was observed upon the character or velocity of the flame with any gas mixture at any stage of the explosion. And inasmuch as the high constant velocity of the explosion wave can be entirely accounted for on the theory of a compression wave liberating the chemical energy as it passes through the gases, there seem as yet to be no experimental grounds for attributing it to the ionising action of electrons.

The Initial Period of "Uniform Movement" or "Inflammation" of Flame through Inflammable Mixtures, and Limits of Inflammability.

Mallard and Le Chatelier, in their classical researches upon the combustion of explosive mixtures, discovered that the propagation of flame, when such a mixture is ignited in a horizontal tube, differs according as whether the ignition occurs near the open or closed end of the tube. In the first case, the flame proceeded for some distance down the tube at a practically uniform and fairly slow velocity, corresponding to the true rate of propagation "by conduction." This period of uniform movement is succeeded by an irregular oscillatory period, in which the flame springs backwards and forwards with increasing amplitudes—finally either dying out altogether or else giving rise to detonation. With certain oxygen mixtures, the initial period of uniform slow velocity was shorter, and appeared to be abruptly succeeded by detonation without the intervention of any oscillatory period. When, however, such mixtures were ignited near the closed end of a horizontal

tube, the forward movement of the flame was continuously accelerated from the beginning, under the influence of reflected compression waves, until detonation was set up. Such, in general, was the sequence of the phenomena that was observed by these distinguished French investigators.

They proceeded to determine experimentally the velocities of the uniform slow movement of the flame in the case of a number of air and combustible gas mixtures, and plotting their results (in cms. per sec.) as ordinates against percentages of inflammable gas as abscissae, they obtained "curves" which were in each case formed of two inclined straight lines converging upwards to a point which represented the composition and flame velocity of the most explosive mixture. And they concluded that the points at which the downward production of the two lines met the zero velocity line would define the upper and lower limits of inflammability for the particular series of gas-air mixtures. Thus the curve they obtain for methane-air mixture was as Fig. 1, showing a maximum velocity of 61 cm. per second for a mixture containing about 12.2 per cent of methane, with lower and upper limits corresponding to 5.6 and 16.7 per cent of methane respectively.

An exact knowledge of the velocities of flame propagation during this initial period of uniform slow movement, as well as of the limits of inflammability for mixtures of various combustible gases and air, is very important from a practical point of view. Makers of apparatus for burning explosive mixtures of gas and air want to know the speed of flame propagation through such mixtures, not only at ordinary temperatures and pressures, but also when the mixtures are heated and used at higher pressures. Also, it would be important to know whether or not, in a case of a complex mixture of various combustible gases and air, when complete composition can be determined by analysis (as, for example, coal-gas and air), the velocity of flame propagation can be calculated from the known velocities for its single components. Unfortunately, although more than thirty years have elapsed since Mallard and Le Chatelier's work was published, the necessary data are still wanting to answer such questions, and anyone who will systematically tackle the problem and carefully work it out in detail will be doing a real service to the gas-using industry. I am hoping shortly to make a beginning with such an investigation in my new department at the Imperial College, London; but the successful and rapid progress of such work will involve considerable financial outlay, as well as organisation and expert direction. Who will help us with the necessary funds?

An accurate knowledge of the behaviour of methane-air mixtures under known variations of conditions is of prime importance from the point of view of the safety of coal mines, and it is rightly occupying the attention of my friend and former collaborator, Dr. R. V. Wheeler, at the Home Office Experimental Station at Eskmeals. From papers which he has already published, as well as from some unpublished results which he has very kindly permitted me to refer to in this address, it is now possible to correct certain errors in Mallard and Le Chatelier's results, and to arrive at a clearer view of the phenomena as a whole.

In the first place, it would appear that the initial "uniform movement" of flame in a gaseous explosion, or, in other words, propagation of the flame from layer to layer by conduction only (as defined by Le Chatelier), is a limited phenomenon, and is only obtained in tubes of somewhat small diameter, wide enough, however, to prevent appreciable cooling of the flame but narrow enough to suppress the influence of convection currents. Moreover, ignition must be either at or within one or two centimetres of the end of the tube, otherwise—particularly with the more rapidly moving flames—vibrations may be set up right from the beginning.

While all methane-air mixtures develop an initial uniform slow flame-movement period when ignited at or near the open end of a horizontal tube, both its linear

duration as well as the flame velocity are not, according to private information which Dr. Wheeler has sent me, independent of the dimensions of the tube. The speed of flame increases with the diameter of the tube, and the linear duration of the uniform period increases with both the diameter and length of the tube up to a certain maximum, after which increased length probably makes no appreciable difference; also for the same tube it varies with the proportion of methane in the explosive mixture, being greater as the speed of the flame diminishes until with the two "limiting" explosive mixtures it appears to last almost indefinitely.

Dr. Wheeler's recent re-determination of the velocities of the flame movement during this initial uniform period for mixtures of methane and air in varying proportions within the limits of inflammability has revealed serious errors in Mallard and Le Chatelier's original results for horizontal tubes of the same diameter as those which Dr. Wheeler has employed. Moreover, Mallard and Le Chatelier's method of determining the composition of the upper and lower limits of inflammability by extrapolation from their curves has been proved to be unwarranted. Dr. Wheeler considers the length of the tubes used by Mallard and Le Chatelier (1 metre only) was insufficient to ensure that the speed measurements of the initial uniform flame movement period were unaffected by the subsequent "vibratory period"; also the methane used by them, prepared as it was from sodium acetate, would obviously be impure.

The most important differences between the latest results published by Dr. Wheeler and those originally determined by Mallard and Le Chatelier, as shown on the accompanying diagram (Fig. 2), are as follows:—

1. According to Wheeler, the limits of inflammability for horizontal propagation of flame in methane-air mixtures, at atmospheric temperature and pressure, correspond to 5.4 and 14.3 per cent methane content respectively, whereas Mallard and Le Chatelier gave 5.6 and 16.7 per cent.
2. Whereas according to Mallard and Le Chatelier the flame velocities for mixtures near the upper and lower limits would gradually approximate to the zero velocity ordinate as the limiting composition was approached, according to Wheeler the velocities for both the upper and lower limiting mixtures are considerable (in each case about 36 cm. per second), and there is an abrupt change from these velocities to zero velocity as the particular limiting composition is passed.
3. Whereas Mallard and Le Chatelier found a maximum velocity of 63 cm. per second for a mixture containing about 12.2 per cent of methane, and rapid falling-off in velocity as this particular composition is deviated from, Wheeler finds a maximum velocity of 110 to 112 cm. per second for a series of mixtures containing from 9.45 to 10.55 per cent of methane. Such differences as are thus disclosed only emphasise the need of a complete experimental revision of the subject.

TABLE II.

Atmosphere.		Methane, per cent.	
Oxygen.	Nitrogen.	Lower limit.	Higher limit.
20.90	79.10	5.60	14.82
17.00	83.00	5.80	10.55
15.82	84.18	5.83	8.96
14.86	85.14	6.15	8.36
13.90	86.10	6.35	7.26
13.45	86.55	6.50	6.70

Messrs. Burgess and Wheeler have recently determined the limits of inflammability of methane when mixed, at atmospheric temperature and pressure, with "atmospheres" of oxygen and nitrogen containing less oxygen

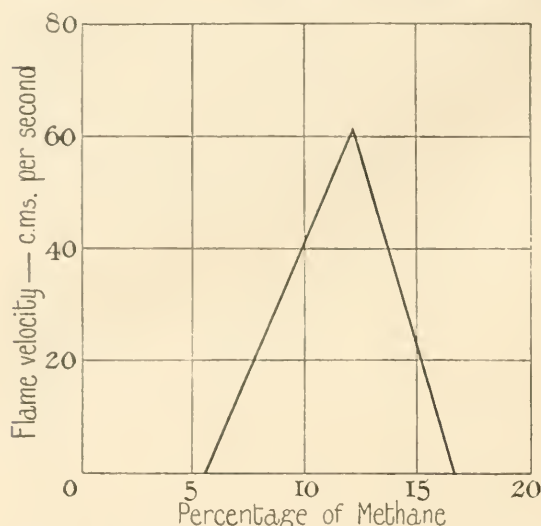


FIG. 1.—Mallard and Le Chatelier's Curve for Velocities of Inflammations on Methane-air Mixtures.

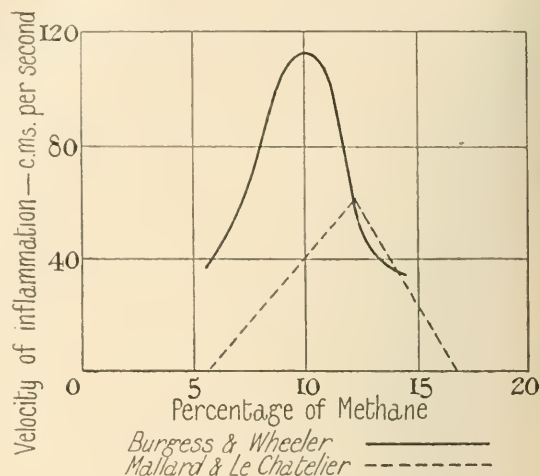


FIG. 2.—Burgess and Wheeler's and Mallard and Le Chatelier's Results Compared.

TABLE III.—Explosion of Mixtures of varying Composition between $2\text{CH}_4 + \text{O}_2$ and $\text{CH}_4 + \text{O}_2$ in Bomb A at Initial Pressure 12.7 Atmospheres.

Experiment No.	10.			11.			12.			13.								
Pressures in atmospheres $\left\{ \begin{array}{l} p_1 \\ p_2 \end{array} \right.$	12.74 15.05 1.18			12.72 18.10 1.42			12.68 17.30 1.36			12.61 14.10 1.12								
p_2/p_1																		
	Per cent.			Partial pressures, atmospheres.			Per cent.			Partial pressures, atmospheres.			Per cent.			Partial pressures, atmospheres.		
Original mixture . $\left\{ \begin{array}{l} \text{CH}_4 \\ \text{O}_2 \end{array} \right.$	67.15	8.55	59.3	7.54	55.75	7.09	50.8	6.40										
	32.85	4.19	40.7	5.18	44.25	5.59	49.2	6.21										
Gaseous products $\left\{ \begin{array}{l} \text{CO}_2 \\ \text{CO} \\ \text{CH}_4 \\ \text{H}_2 \end{array} \right.$	3.10	0.47	2.70	0.49	3.85	0.67	7.45	1.05										
	25.40	3.83	35.60	6.44	37.25	6.44	38.50	5.44										
	16.60	2.50	4.65	0.84	2.25	0.39	Nil	Nil										
	54.90	8.26	57.05	10.32	56.65	9.80	54.05	7.60										
Units in $\left\{ \begin{array}{l} \text{original mixture} \\ \text{gaseous products} \end{array} \right.$..	C. 8.55 H. 17.10 O. 4.19	C. 7.54 H. 15.08 O. 5.18	C. 7.09 H. 14.18 O. 5.59	C. 6.40 H. 12.80 O. 6.21														
	6.80 13.26 2.38	7.77 12.00 3.71	7.50 10.58 3.89	6.49 7.60 3.77														
Difference $\left\{ \begin{array}{l} \text{Atmospheres} \\ \text{Per cent} \end{array} \right.$..	1.70 3.84 1.81	— 3.08 1.47	— 3.60 1.70	— 5.20 2.44														
	20 43.2	— 28.4	— 30.4	— 38.2														
Ratio $\frac{\text{CO} \times \text{OH}_2}{\text{CO}_2 \times \text{H}_2}$ in products	3.65			3.75			3.43			3.4								
Remarks	Explosions almost inaudible; carbon deposited.			Explosions distinctly audible.			No carbon deposited.			Very violent explosion with sharp metallic click. No carbon deposited.								

than ordinary air. From their results (Table II.) it would appear that as the oxygen content of the atmosphere is reduced the limits of inflammability are narrowed until they coincide when the oxygen content falls below 13.3 per cent, which means that an atmosphere containing 13.3 or less per cent of oxygen is truly extinctive for a methane flame at ordinary pressures.

Behaviour of Weak Mixtures of Gases and Air.

My review of this part of the subject would be incomplete without a reference to some interesting observations which have been made by Dr. H. F. Coward and co-

workers at the Manchester School of Technology upon the behaviour of weak mixtures of various inflammable gases and air at or just below the lower limit of inflammability in each case (*Trans. Chem. Soc.*, 1914, cv., 1859). Their principal experiments were carried out in a rectangular box of 30 cm. square section and 1.8 metres length, with two opposite sides of wood and the other two of plate glass. The box was placed in an upright position, the bottom being water-sealed and the top closed, with a suitable igniting device placed near the bottom. They have shown that caps or vortex rings of flame may be projected for some distance upwards from the source of

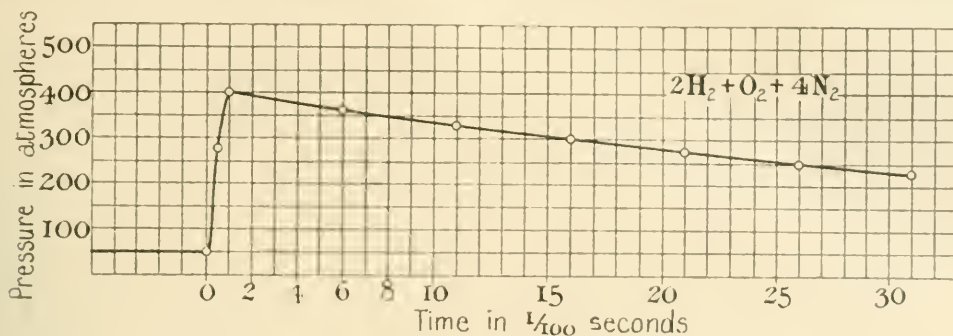


FIG. 3.

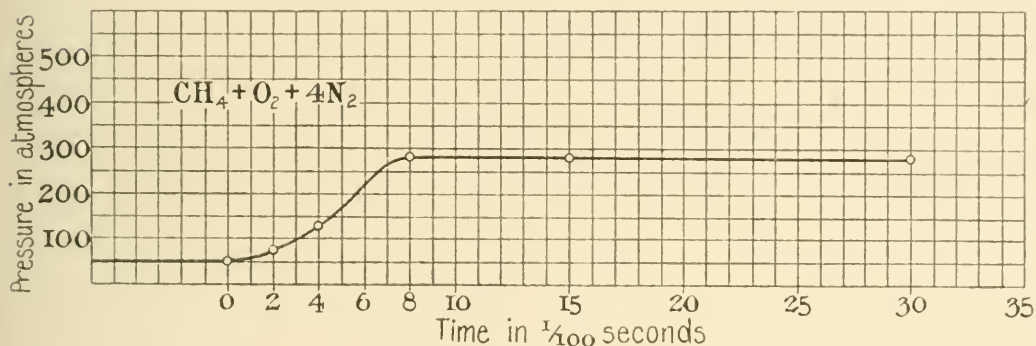


FIG. 4.

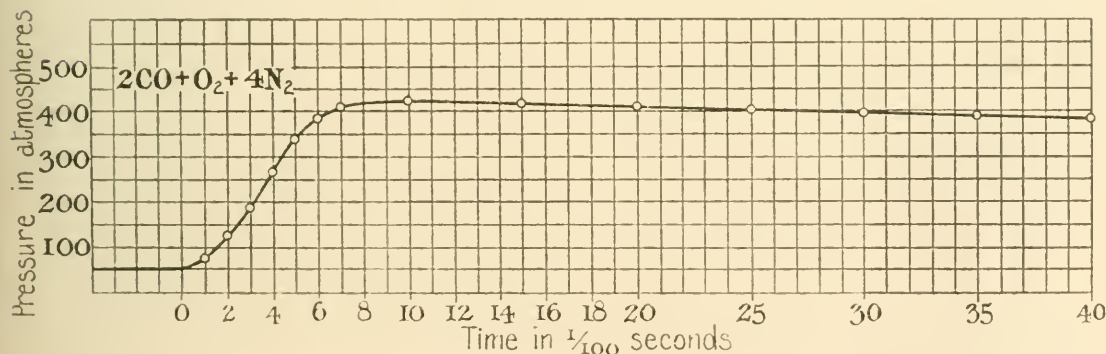


FIG. 5.

ignition—sometimes apparently for an indefinite distance—without igniting the whole of the combustible mixture. In such mixtures there may be an indefinite upward slow propagation of flame, together with incompleteness of combustion, much of the combustible mixture remaining unburnt, and the question very naturally arises as to how the term "inflammability" should be scientifically defined. Dr. Coward has argued with some force that a gaseous mixture should not be termed "inflammable" at a given temperature and pressure unless it will propagate flame indefinitely, the unburnt portion being maintained at that temperature and pressure. Inflammability thus defined would be a function of the temperature, pressure, and composition of a particular mixture only, and would be independent of the shape and size of the containing vessel, and, provided that it is kept in mind that for each particular mixture at a given temperature and pressure a certain minimum igniting energy and intensity is requisite, I am inclined to agree with the definition; also there is a possibility that in a mixture just at or very near one or

other of the limits of inflammability flame may be propagated upwards but not downwards.

From his experiments Dr. Coward has assigned the following as the lower limits of inflammability of hydrogen, methane, and carbon monoxide respectively in air at atmospheric temperature and pressure:—

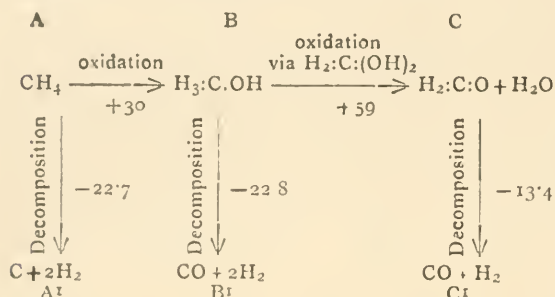
	Per cent.
Hydrogen	4.1
Methane	5.3 (a)
Carbon monoxide	12.6

- (a) Too much stress need not be laid upon the difference between this number and the 5.6 per cent given by Dr. Wheeler (*loc. cit.*), because Dr. Coward himself admits that the flames of mixtures containing from 5.3 to 5.6 per cent of methane are very sensitive to shock, while a 5.6 per cent mixture will always propagate flame indefinitely, even when there is a moderate disturbance. The conditions must be exceedingly tranquil to prevent extinction in the other cases.

Combustion of Hydrocarbons and Relative Affinities of Methane, Hydrogen, and Carbon Monoxide respectively for Oxygen in Flames.

Under the title of "Gaseous Combustion at High Pressure" I have recently published, in conjunction with various collaborators (Messrs. Hamilton Davies, H. H. Gray, H. H. Henstock, and J. B. Dawson), a further instalment of my researches on the mechanism of hydrocarbon combustion (*Phil. Trans. Roy. Soc.*, 1915, A, ccxv., 275), and I may, perhaps, be allowed to draw your attention to certain new points which have arisen in connection therewith.

A detailed study of the behaviour of mixtures of methane and oxygen, of composition ranging between $2\text{CH}_4 + \text{O}_2$ and $\text{CH}_4 + \text{O}_2$, when exploded in steel bombs at initial pressures of 12.7 atmospheres (see Table III.), has shown it to be consistent with the "hydroxylation" theory of hydrocarbon combustion which I put forward some years ago as the result of my previous work. The following scheme seems to interpret correctly the chemical and thermal changes involved in the initial stages of the explosive combustion of methane.



The principal experimental facts which this—or, indeed, any alternative—scheme must explain are:—

1. That whenever mixtures of composition between $2\text{CH}_4 + \text{O}_2$ and $\text{CH}_4 + \text{O}_2$ are exploded under pressure, a considerable proportion of the original oxygen appears as steam in the products.
2. That there is a marked minimum in the proportion of such oxygen as the composition of the original mixture approximates to $3\text{CH}_4 + 2\text{O}_2$.
3. That there is a total cessation of any separation of carbon (which is very marked with mixtures $2\text{CH}_4 + \text{O}_2$) alter the proportion of oxygen in the original mixture attains or exceeds the limit $3\text{CH}_4 + 2\text{O}_2$.

Now if, as I believe, the initial interaction of methane and oxygen is at all temperatures essentially a "hydroxylation" process, accompanied by the decomposition (more or less rapid according to the temperature) of the primarily formed hydroxylated molecules, a consideration of the chemical and thermal aspects of the process will point to certain possibilities which are, indeed, actually realised in fact.

In the first place monohydroxymethane (methyl alcohol) $\text{CH}_3\cdot\text{OH}$ is known to decompose at high temperature, yielding carbon monoxide and oxygen, without any separable separation of carbon or formation of steam. $\text{CH}_3\cdot\text{OH} = \text{CO} + 2\text{H}_2$; also the very unstable dihydroxymethane, $\text{H}_2\text{C}\cdot\text{C}\cdot(\text{OH})_2$, would yield formaldehyde and steam, $\text{H}_2\text{C}\cdot\text{C}\cdot(\text{OH})_2 = \text{H}_2\text{C}\cdot\text{C}\cdot\text{O} + \text{H}_2\text{O}$, and the formaldehyde would in turn decompose into carbon monoxide and hydrogen, $\text{H}_2\text{C}\cdot\text{C}\cdot\text{O} = \text{CO} + \text{H}_2$, without any deposition of carbon whatever.

If now the thermal consequences of such facts be considered, it would appear (1) that were the oxidation of methane to $\text{H}_3\text{C}\cdot\text{C}\cdot\text{OH}$ (A to B in the scheme) accompanied by thermal decomposition at this stage (B to B'), the net heat evolution would be $(30 - 22.8) = 7.2$

kilograms. Centigrade units, whereas (2) of the same amount of oxygen reacted in such a way that there was a "non-stop" run through the monohydroxy to the dihydroxy stage, with decomposition at the point (A to C and C to C'), the corresponding net heat evolution would be $\frac{1}{2}(30 + 59 - 13.4) = 37.8$ units, or about five times as much as in (1). Hence, there would always be a strong tendency for such a non-stop run from A to C through B without any decomposition occurring at B, and such would always occur whenever the oxygen present in the original mixture attained the equimolecular proportion $\text{CH}_4 + \text{O}_2$.

Again, if the original mixture contained only one-half such proportion of oxygen ($2\text{CH}_4 + \text{O}_2$), there would still be a decided preference for an oxidation of half of the methane by a non-stop run A to C through B rather than an oxidation of the whole of the methane to B only, the other half of the methane remaining unchanged or undergoing thermal decomposition into its elements, $\text{CH}_4 = \text{C} + 2\text{H}_2$ (A to A'); also the latter process would use up no more of the energy developed from the oxidation than would be required for the decomposition of a corresponding quantity of $\text{H}_3\text{C}\cdot\text{C}\cdot\text{OH}$ at stage B (B to B'). Hence, when such a mixture $2\text{CH}_4 + \text{O}_2$ is exploded under pressure the formation of carbon and its oxides, hydrogen, and considerable quantities of steam may be expected, which is precisely what actually occurs.

When, however, the proportion of oxygen in the original mixture reaches the limit $3\text{CH}_4 + 2\text{O}_2$, while it is still insufficient to oxidise the whole of the hydrocarbon to the dihydroxy stage, there is enough of it to prevent any methane remaining unoxidised to at least the monohydroxy stage, and therefore, seeing that the affinity of methane for oxygen far exceeds those of either hydrogen or carbon monoxide, it is to be expected that no substantial proportion of the original methane would escape oxidation to either the mono or the dihydroxy stage. But inasmuch as not more than about one-third of the original methane could in the circumstances be transformed into the dihydroxy stage, it follows that a considerable amount of thermal decomposition at the monohydroxy stage would occur.

If this view is correct it follows that there should be an entire suppression of carbon deposition at or about the $3\text{CH}_4 + 2\text{O}_2$ ratio, and also that with this particular mixture a smaller proportion of the original oxygen should appear as steam in the products than would be the case with either the $2\text{CH}_4 + \text{O}_2$ or the $\text{CH}_4 + \text{O}_2$ mixture, which again is precisely what we find.

In considering the question of the explosive combustion of hydrocarbon, it is important to distinguish between (1) the primary oxidation of the hydrocarbon, which is an exceedingly rapid process, and is probably completed during the short interval between ignition and the attainment of maximum pressure, and (2) certain probable secondary interactions where influence may extend far into the subsequent cooling period, for it is only this latter which would be affected by variations in the rate of cooling down from the maximum temperature. Such secondary interaction may include the reversible change $\text{CO} + \text{OH}_2 = \text{CO}_2 + \text{H}_2$, and in cases where carbon is deposited as the result of the decomposition of primary oxidation products the interaction of steam and carbon $\text{C} + \text{OH}_2 = \text{CO} + \text{H}_2$. In this connection I may draw attention to the recently published work of G. W. Andrew (*Trans. Chem. Soc.*, 1914, cv., 444), one of my former pupils and collaborators, on the "Water-Gas Equilibrium in Hydrocarbon Flames," which proves that in a system containing only CO_2 , CO , H_2 , H_2O , rapidly cooling down from the high temperatures prevailing in hydrocarbon flames, the equilibrium ratio $\text{CO} \times \text{OH}_2 / \text{CO}_2 \times \text{H}_2$ adjusts itself automatically with the temperature until a point between 1500° and 1600°C . on the cooling curve is reached (corresponding to a value $K = 4.0$ approximately), after which no further readjustment

occurs. He also found that this adjustment of equilibrium is not greatly influenced even when relatively large quantities of methane and carbon are found in the final products.

I am able from my own experiments to confirm Andrew's conclusions in all cases where the initial firing pressure is insufficient to set up detonation, but in cases where both detonation and separation of carbon occur my results undoubtedly indicate an appreciable intervention of the separated carbon during the cooling period. There is nothing in my results, however, suggestive of an appreciable intervention of methane.

The fact that the primary oxidation of methane usually involves a direct transition from $\text{CH}_4 + \text{O}_2$ to $\text{CH}_2(\text{OH})_2$, which latter breaks up into, ultimately, $\text{CO} + \text{H}_2 + \text{H}_2\text{O}$, without deposition of carbon, opened up the possibility of instituting a direct experimental comparison between the relative affinities of methane and hydrogen for oxygen in explosion, by exploding a series of mixtures $\text{CH}_4 + \text{O}_2 + x\text{H}_2$ in which the hydrocarbon and oxygen were initially present in as nearly as possible equimolecular proportions, but in which x (the volume ratio of H_2 to CH_4) was varied between 2 and 8, and determining (1) the oxygen distribution on explosion when $x=2$, and (2) the influence upon such distribution of successive equal increments of x up to 8 (Table IV.).

TABLE IV. — Oxygen Distribution of Mixtures $\text{CH}_4 + \text{O}_2 + x\text{H}_2$ are exploded.

x		2.	4.	6.	8.
		Per cent.	Per cent.	Per cent.	Per cent.
Bomb A	O_2 to CH_4	95.34	81.0	54.9	31.4
	O_2 to H_2	4.66	19.0	45.1	68.6
Bomb B	O_2 to CH_4	97.1	91.0	72.6	—
	O_2 to H_2	2.9	9.0	27.4	—

Ever since Davy's experiments in flame, the combustibility of hydrogen has been erroneously considered to be superior to that of methane; but, on the other hand, my previous researches upon hydrocarbon combustion have shown (1) that in slow combustion in borosilicate glass bulbs at temperatures between 300° and 400°C ., methane, ethane, and acetylene are all oxidised at a much faster rate than in hydrogen or carbon monoxide, and also (2) that, in exploding such mixtures as $\text{C}_2\text{H}_4 + \text{H}_2 + \text{O}_2$ or $\text{C}_2\text{H}_2 + 2\text{H}_2 + \text{O}_2$, the hydrocarbon is burnt in preference to hydrogen facts which are at variance with any notion of the superior affinity of hydrogen for oxygen in flames.

My further experiments upon the relative affinities of methane and hydrogen for oxygen in explosives were carried out at high initial pressures in two special steel bombs — namely, A, with a cylindrical explosion chamber, 8 ins. long and 1 in. in diameter (capacity = circa 103 cc.); and, B, with a spherical cavity 3 in. in diameter (capacity = circa 275 cc.). The ratio of wall surface of the explosion chamber in the case of bomb A would thus be about 2.75 times that of bomb B. The mean results for the distribution of oxygen between methane and hydrogen in the two sets of experiments were as in the table.

It is at once quite evident, from the results with the mixture $\text{CH}_4 + \text{O}_2 + 2\text{H}_2$, that the affinity of methane is at least twenty to thirty times greater than that of hydrogen for oxygen in explosion flames. The actual distribution of oxygen when a particular mixture is exploded, is undoubtedly influenced to some extent by the walls of the containing vessel, but not, so far as I have been able to ascertain, by the absolute initial pressure. Moreover, it is evident that the influences of successive increases in x , the volume ratio of H_2 to CH_4 in the mixture exploded, upon the actual oxygen distribution for a given explosion, is proportionate to x_2 , which can hardly mean other than that in explosion flames hydrogen is directly burnt to steam, and not, as many have supposed *via* the intermediate formation of hydrogen peroxide.

A similar series of experiments with mixtures

$\text{CH}_4 + \text{O}_2 + x\text{CO}$ show that, while it is impossible, owing to circumstances which I need not here detail, to deduce, even approximately, any numerical relation between the affinities of methane and carbon monoxide for oxygen in flames, yet we can confidently say that the affinity of the hydrocarbon is again vastly the superior, although carbon monoxide is apparently more effective than hydrogen in pulling away oxygen from the predominating attraction of methane.

Having thus satisfactorily disposed of the question of the relative affinities of the three gases for oxygen in explosion flames, it remained to prove whether or not such chemical factors determine the ratio of attainment of maximum pressure in explosions, by exploding mixtures of each of the three combustible gases, with air, in such proportions as correspond with the primary oxidation — namely, (1) $\text{CH}_4 + \text{O}_2 + 4\text{N}_2$, (2) $2\text{H}_2 + \text{O}_2 + 4\text{N}_2$, and (3) $2\text{CO} + \text{O}_2 + 4\text{N}_2$ — at initial pressures of 45 to 50 atmospheres in the spherical bomb B, to which was attached a Petavel recording manometer with its optical accessories.

The pressure records which are reproduced in the following diagrams (Figs. 3, 4, and 5), in which pressures in atmospheres are plotted against time in seconds, prove conclusively the absence of any direct relation between the actual rate at which the potential energy of an explosive mixture is transferred on explosion as sensible heat to its products, and the magnitude of the chemical affinity between its combining constituents. This is hardly to be wondered at, seeing the extreme rapidity of chemical interaction at high temperature as compared with the rate at which the liberated heat be communicated to, and uniformly distributed among, the products by ordinary physical processes. Attention may be drawn to the extreme slowness of the cooling in each case after the attainment of maximum pressure. This has also been observed by previous workers in other similar cases of gaseous explosions. This was particularly marked in the case of the methane-air mixture, in which there was hardly any appreciable cooling during an interval of 0.22 seconds after the attainment of maximum pressure (in 0.08 second), a circumstance which may be due in part to the combustion taking place in well-defined chemical stages, and in part also to the operation of the exothermic secondary interaction between carbon monoxide and steam during the cooling period. On the other hand, the curve for the hydrogen-air mixture, where the combustion to steam is a direct and comparatively simple transaction, suggests that the attainment of maximum pressure is succeeded by a period of gradual cooling uninfluenced by chemical combination.

(To be continued).

STUDIES IN THE STEREOCHEMISTRY OF QUINQUEVALENT NITROGEN.*

RESOLUTION OF THE ASYMMETRIC QUATERNARY AMMONIUM COMPOUNDS.

By SHIGERU KOMATSU.

(Continued from p. 210).

In another experiment, pure *laevo* methyl allyl phenyl benzyl ammonium *laevo*-camphorsulphonate was prepared from the externally compensated ammonium iodide and silver *laevo*-camphorsulphonate; it consisted of white needles, which were found to have the melting-point $162-163^\circ$ and the specific rotatory power $[\alpha]_{\text{D}}^{25} = -46.69^\circ$.

Now, the author, expecting that stereoisomers may exist in the active forms of the ammonium compound, has undertaken the resolution of γ methyl allyl phenyl benzyl ammonium iodide by means of anhydrous silver dextro-

* Memoirs of the College of Science, Kyoto Imperial University, 1915, i, No 3.

TABLE II.

α -Compounds.	Pope and Harvey.	Author.
$d\text{-(CH}_3\text{)(C}_3\text{H}_5\text{)(C}_6\text{H}_5\text{)(C}_7\text{H}_7\text{)N.C}_{10}\text{H}_{15}\text{SO}_4$	171—173° $\alpha_D^{25} = +16.6$	164—163° $\alpha_D^{25} = +16.71^a$
$d\text{-(CH}_3\text{)(C}_3\text{H}_5\text{)(C}_6\text{H}_5\text{)(C}_7\text{H}_7\text{)N.I}$	147° $\alpha_D^{17} = +55.1$	135—136° $\alpha_D^{25} = +68.28^\circ (a)$ $\alpha_D^{25} = +51.72^\circ (b)$
$d\text{-(CH}_3\text{)(C}_3\text{H}_5\text{)(C}_6\text{H}_5\text{)(C}_7\text{H}_7\text{)N.Br}$	165—167° $\alpha_D^{16.2} = +64.1^\circ (a)$	155—156° $\alpha_D^{25} = +67.44^\circ (b)$
$d\text{-(CH}_3\text{)(C}_3\text{H}_5\text{)(C}_6\text{H}_5\text{)(C}_7\text{H}_7\text{)NI.HgI}_2$	124—125° $[\alpha]_D^{14} = +24.3$	119—120° $[\alpha]_D^{25} = +24.86^\circ$
$d\text{-(CH}_3\text{)(C}_3\text{H}_5\text{)(C}_6\text{H}_5\text{)(C}_7\text{H}_7\text{)NCI}_2\text{PtCl}_4$	166°	149—150°
$l\text{-(CH}_3\text{)(C}_3\text{H}_5\text{)(C}_6\text{H}_5\text{)(C}_7\text{H}_7\text{)N.C}_{10}\text{H}_{15}\text{SO}_4$	171—173° $\alpha_D^{19} = -45.5$	162—163° $\alpha_D^{25} = -16.59^\circ$
$l\text{-(CH}_3\text{)(C}_3\text{H}_5\text{)(C}_6\text{H}_5\text{)(C}_7\text{H}_7\text{)NI}$	147° $[\alpha]_D^{17} = -53.4^\circ (a)$	134—135° $\alpha_D^{25} = -51.34^\circ (b)$
$l\text{-(CH}_3\text{)(C}_3\text{H}_5\text{)(C}_6\text{H}_5\text{)(C}_7\text{H}_7\text{)NI.HgI}_2$	125—126° $[\alpha]_D^{14.5} = -23.5$	119—120° $\alpha_D^{25} = -24.12$
γ -Compounds.	Author.	
$d\text{-(CH}_3\text{)(C}_3\text{H}_5\text{)(C}_6\text{H}_5\text{)(C}_7\text{H}_7\text{)N.S}_{10}\text{H}_{15}\text{SO}_4$	Melting-point. 163°	$[\alpha]_D^{25}$ +58.61
$d\text{-(CH}_3\text{)(C}_3\text{H}_5\text{)(C}_6\text{H}_5\text{)(C}_7\text{H}_7\text{)N.I}$	134—135°	+73.98° (a) +65.54° (b)
$d\text{-(CH}_3\text{)(C}_3\text{H}_5\text{)(C}_6\text{H}_5\text{)(C}_7\text{H}_7\text{)N.Br}$	155—156°	+81.80°
$d\text{-(CH}_3\text{)(C}_3\text{H}_5\text{)(C}_6\text{H}_5\text{)(C}_7\text{H}_7\text{)N.I.HgI}_2$	120—121°	+39.51
$d\text{-(CH}_3\text{)(C}_3\text{H}_5\text{)(C}_6\text{H}_5\text{)(C}_7\text{H}_7\text{)N.Cl}_2\text{PtCl}_4$	148—149°	
$l\text{-(CH}_3\text{)(C}_3\text{H}_5\text{)(C}_6\text{H}_5\text{)(C}_7\text{H}_7\text{)N.C}_{10}\text{H}_{15}\text{SO}_4$	163—164°	-56.21°
$l\text{-(CH}_3\text{)(C}_3\text{H}_5\text{)(C}_6\text{H}_5\text{)(C}_7\text{H}_7\text{)N.I}$	135—135.5° ^a	-63.15°
$l\text{-(CH}_3\text{)(C}_3\text{H}_5\text{)(C}_6\text{H}_5\text{)(C}_7\text{H}_7\text{)N.I.HgI}_2$	120°	-39.60°
	(a) In chloroform.	(b) In alcohol.

camphorsulphonate, and γ dextro-methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate obtained and recrystallised from acetone, consisted of white needles which melt at 162°, and its mean specific rotatory power in an aqueous solution was found to be $[\alpha]_D^{25} = +58.46^\circ$.

Since the specific rotatory power of the γ form is not altered by recrystallisation, it is noteworthy that the pure sample of α methyl allyl phenyl benzyl ammonium compound has lower specific rotatory power than that of the γ isomer.

Now, the author has to ascribe the difference of the specific rotatory powers in α and γ isomerides to the different configurations of the atomic groups in their molecules.

For the confirmation of this view the author has conducted the experiment to be described below.

In the experiment the racemic dextro-camphorsulphonate was macerated with ethyl acetate according to Pope and Harvey (*loc. cit.*), and the purified γ dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate used had the properties already stated, *i.e.*, the white needle-shaped crystals melted at 163°, and the specific rotatory power of the well purified sample in an aqueous solution was found to be $[\alpha]_D^{25} = +58.76^\circ$ as the mean value.

To the crude γ laevo methyl allyl phenyl benzyl ammo-

nium iodide obtained from the impure dextro methyl allyl phenyl benzyl ammonium dextro camphorsulphonate, an equimolecular silver dextro-camphorsulphonate was added, and the reaction product was subjected to fractional crystallisation, using acetone as the solvent. And pure γ laevo methyl allyl phenyl benzyl ammonium laevo-camphorsulphonate thus obtained was found to be white needle-shaped crystals which had the properties similar to those of the enantiomorphous compound; it melted at 163—164°, and its specific rotatory power was shown to be $[\alpha]_D^{25} = 56.21$, which is lower than that of its enantiomorph.

γ laevo methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate, prepared from racemic γ methyl allyl phenyl benzyl ammonium iodide and silver laevo camphorsulphonate, was observed to have the same melting-point, the same specific rotatory power, and the same crystalline form as those of the compound above mentioned.

The author has prepared several other optically active ammonium compounds of the α and γ series, and compared their melting-point and specific rotatory power in alcohol or chloroform solutions with those of the same substances stated by Pope and Harvey (*loc. cit.*), as shown in Table II.

From the experimental results so far obtained the following conclusions are drawn:—

1. The asymmetrical ammonium compounds prepared by the author may directly resolve into optically active antipodes by means of optically active acids.

2. Whilst the melting-points of the same optically active compounds obtained by the same method do not agree with those of the other investigators their specific rotatory powers are concordant to each other.

3. In the optically active methyl allyl phenyl benzyl ammonium compounds there exist optical isomers in α and γ forms, which possess the same melting-points but different specific rotatory powers.

The optically active acids used for the resolution were dextro-camphorsulphonic, laevo-camphorsulphonic, and dextro-bromocamphorsulphonic acids. And dextro-camphorsulphonic acid was prepared according to Reyckler (*Bull. Soc. Chim.*, 1898, xix., 120) from Japan camphor purified by sublimation and by treating with concentrated sulphuric acid and acetic anhydride, and it was obtained in the form of hygroscopic crystals melting at 192–193°, showing its specific rotatory power as $[\alpha]_D^{25} = +23.14^\circ$ in its aqueous solution. Laevo-camphorsulphonic acid used in the experiment was prepared according to Pope and Harvey (*Journ. Chem. Soc.*, 1901, lxxix., 76, 80) from laevo-borneol from Kahlbaum, and its melting-point was found to be 190° and the specific rotatory power of its ammonium salt in the aqueous solution to be $[\alpha]_D^{25} = -21.35^\circ$. Dextro-bromocamphorsulphonic acid obtained according to the method suggested by Marsh and Cousins (*Ibid.*, 1891, lix., 966) from dextro-bromocamphor crystallised from methyl alcohol and chlorosulphonic acid, was purified by converting it into the ammonium salt which possessed the specific rotatory power, $[\alpha]_D^{25} = +85.54^\circ$, in an aqueous solution.

(To be continued).

RADIOMETRIC MEASUREMENTS OF THE IONISATION CONSTANTS OF INDICATORS.*

By E. J. SCHAEFFER, M. G. PAULUS, and HARRY C. JONES.

(Continued from p. 209).

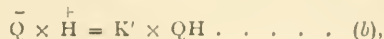
Theoretical Discussion.—The Ostwald theory of indicators (*Lehrbuch der All. Chem.*, 1891, i., 799), explaining, first, the cause of colour, and, second, the difference in sensitiveness of various indicators towards different acids and bases, has been found to be inadequate. Concerning the latter, which is by far the most important side of the indicator question, the Ostwald interpretation is substantially correct. But in consideration of well-known relations between the colour and structure of organic compounds, and of the researches of Bernthsen (*Chem. Zeit.*, 1892, p. 1956; also Friedländer, *Ber.*, 1893, xxvi., 172, 2258), Nietz and Burckhart (*Ber.*, 1897, xxx., 175), Hanitzsch (*Ber.*, 1899, xxxii., 583, 3085), and others, it has been found necessary to modify the Ostwald view as to the cause of colour. The facts and relations brought out by these investigations have been correlated and interpreted by Stieglitz in the so-called chromophoric theory of colour (*Journ. Am. Chem. Soc.*, 1903, xxv., 1112). A. A. Noyes (*Journ. Am. Chem. Soc.*, 1910, xxxii., 815) in a quantitative application of the theory of indicators to volumetric analysis, has also fully explained the significance of the chromophoric theory. According to this theory it is necessary to consider an indicator solution as containing a mixture of two tautomeric substances of different structural types. The ionisation constants of the two forms and the equilibrium relations between them are such that when the indicator exists as a slightly ionised acid or base, one form is present in greatly pre-

dominating quantity. The other form largely predominates when the indicator exists as a highly ionised salt.

Considering phenolphthalein, the ionisation constant K_i , according to the Ostwald conception, is expressed by the simple equilibrium equation:—



The chromophoric theory, as Stieglitz has shown (*loc. cit.*), requires two such equations (a) and (b):—



where k is the stability constant expressing the equilibrium relation between the two tautomeric acids. The acid represented by LH is assumed to be a pseudo- or an extremely weak acid, and that by QH is the true acid. Its ionisation constant K' is of such a magnitude that the quinoid salt is formed in greatly predominating quantity in the presence of alkalis, the stability constant k acting so as to maintain the equilibrium relation between the two tautomeric acids. The ionisation constant for phenolphthalein is the product of the stability constant k , and the ionisation constant K' of the acid QH; or combining a and b and incorporating k and K' into K_i , we have—



The above equations illustrate the fundamental differences between the two colour theories, and accepting the Stieglitz interpretation of K_i according to Equation 2, the theory underlying the calculation of the dissociation constant of methyl-orange from radiometric measurements will be discussed.

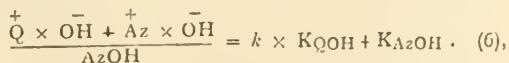
Methyl-orange is in reality a weak base. Noyes (*Journ. Am. Chem. Soc.*, 1910, xxxii., 818) has deduced a general expression for the equilibrium relations of any pair of tautomeric bases and their ions. This deduction involves three fundamental equations. Expressing the equilibrium relation k , between the quinoid and azo-base, it being understood that the symbols represent grm.-molecular or grm. ionic concentrations, we have—



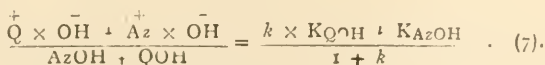
The quinoid base and the azo-base are also in equilibrium with their ions according to 4 and 5:—



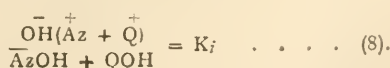
Multiplying 3 by 4 and adding 5 to the product, we obtain—



and substituting in the denominator for AzOH its value $\frac{\text{AzOH} + \text{QOH}}{1 + k}$ it follows that—



Letting the above equal K_i , we have—



* This investigation was carried out with the aid of a grant from the Carnegie Institution of Washington generously awarded to H. C. Jones. From *Journal of the American Chemical Society*, xxxvii., No. 4.

Noyes has called attention to the fact that for a satisfactory two-colour indicator such as methyl-orange, the sum of the two tautomeric bases ($\text{AzOH} + \text{QOH}$), must be substantially equal to AzOH , and that the sum of the two ions ($\text{Q}^+ + \text{Az}^+$) must be substantially identical with Q^+ . It therefore follows—

$$\frac{\text{OH}^- \times \text{Q}^+}{\text{AzOH}} = K_1 \quad \dots \quad (9),$$

where K_1 expresses the equilibrium relations of the two tautomeric bases and their ions, and is substantially the equation derived by Stieglitz (*Journ. Am. Chem. Soc.*, 1903, xxv., 1112).

Combining Equation 9 with that of the ion product of water $\text{H}^+ \times \text{OH}^- = K_w$, we get—

$$\frac{\text{H}^+ \times \text{AzOH}}{\text{Q}^+} = \frac{K_w}{K_1} = K_{(\text{hydrolysis})} \quad \dots \quad (10),$$

which is in reality the familiar equation of Walker ($\frac{\text{acid} \times \text{base}}{\text{salt}} = k$) (*Zeit. Physik. Chem.*, 1889, iv., 324).

Having determined the hydrolysis constant according to Equation 10, the ionisation constant K_1 of methyl-orange as a base can readily be obtained. The procedure, then, is to determine by radiometric measurements, the concentrations of Q^+ , H^+ , and AzOH in solutions of methyl-orange containing varying amounts of these constituents. A method was developed whereby the concentration of the quinoid ions Q^+ in Equation 10 could be determined from the light transmitted by the indicator solutions. The percentage transmissions for these solutions were given by the radio-micrometer deflections. The method will be made clear by the following theoretical considerations applied to methyl-orange.

If we consider light to pass through an absorbing solution of depth l , the solvent itself having no absorption, the rate of change of intensity dI is given by—

$$dI = -kIdl \quad \dots \quad (11),$$

The constant k depends only on the wave length of light and the nature of the absorbing medium. If I_0 denotes the intensity of the incident light, then, when $l = 0$, $I_0 = I = \text{constant}$. Integrating, the intensity of the transmitted light I given by an absorbing solution of depth l and concentration c is—

$$I = I_0 e^{-kcl} \quad \dots \quad (12),$$

If the solution has a second absorbing component, the light transmitted by it will be—

$$I_1 = I_0 e^{-k'l'c'} \quad \dots \quad (13),$$

Since the total transmission is the product of the separate transmissions, we have for the actual percentage transmission of a solution containing two absorbing components such as methyl orange—

$$I/I_0 = e^{-kcl - k'l'c'}; \text{ or } \ln(I/I_0) = -kcl - k'l'c'. \quad (14),$$

Since the depth of solution was maintained constant (20 mm.), the above equation becomes—

$$\ln(I/I_0) = -Kc - K'c' \quad \dots \quad (15),$$

Applying this equation to methyl-orange, let c represent the concentration of the quinoid salt or Q in Equation 10, and c' that of the azo-base. If T is the total quantity of methyl orange in solution, then $c' = (T - c)$; or since a dihasic acid was used, viz., sulphuric acid, $c' = (T - 2c)$. When a pure solution of methyl-orange is slightly acidified with sulphuric acid, and not all of the azo-base converted

into the quinoid salt, both c and c' are present. The light transmitted by such a solution will be—

$$\ln(I/I_0) = -Kc - K'(T - 2c) \quad \dots \quad (16),$$

In a pure aqueous solution of methyl-orange, or one containing an excess of alkali, $c = 0$, therefore Equation 15 reduces to—

$$\ln(I/I_0)' = -K'c' = -K'T \quad \dots \quad (17),$$

If to a solution of methyl-orange sufficient sulphuric acid is added to convert all of the azo-base into the quinoid salt and completely suppress hydrolysis, $c' = 0$, and Equation 15 becomes—

$$\ln(I/I_0)'' = -Kc = -KT/2 \quad \dots \quad (18),$$

From Equations 16, 17, and 18, K and K' can be eliminated, and solving for c we obtain—

$$c = \frac{T[\ln(I/I_0) - \ln(I/I_0)']}{2[\ln(I/I_0)'' - \ln(I/I_0)']} \quad \dots \quad (19),$$

In the above equation $(I/I_0)'$ is the percentage transmission for the solution of pure methyl-orange for some given wave-length of light; $(I/I_0)''$ the percentage transmission of the solution containing an excess of acid for the same wave-length, and (I/I_0) the percentage transmission for the same wave-length of the solution whose quinoid salt concentration c , is to be determined.

Returning now to the fundamental hydrolysis equation for methyl-orange previously derived—

$$\frac{\text{H}^+ \times \text{AzOH}}{\text{Q}^+} = \frac{K_w}{K_1}$$

we can readily insert the proper values knowing the total concentration of methyl-orange T , and having determined by radiometric means the quinoid salt concentration c . Q

is equal to $2c$. $\text{AzOH} = c' = T - 2c$. H^+ is given by $2(T' - c)$ where T' represents the total quantity of acid added. It is assumed that the dissociation of these extremely dilute solutions is practically complete. The sulphonic acid group can have but little effect upon the hydrogen ion concentration, since benzenesulphonic acid (Carnegie Institution of Washington, 1912, *Publication* No. 170, p. 128) is as strong as sulphuric acid, being dissociated at 25° to the extent of 90 per cent for a dilution $v = 32$. As Stieglitz (*Journ. Am. Chem. Soc.*, 1903, xxv., 1117) has pointed out, the whole behaviour of methyl-orange is that of a very weak base, and the elimination of the sodium sulphonate group from it leaves dimethylaniline azobenzene, which shows all the characteristics of methyl-orange as an indicator.

It will be noticed from Equation 10 that it is necessary to know the ionisation constant for water, before the constant for the indicator can be calculated from its hydrolysis constant. The generally accepted value of K_w at 25° is 1.2×10^{-14} . It was desired to know the value of the constant at 20° , since, unless otherwise stated, it was at this temperature that all measurements were made. Owing to the large value of the heat of ionisation of water, the value of its ionisation constant is much less at 20° than at 25° . Just what this change is may be calculated from the well-known van't Hoff formula—

$$\ln \frac{K_1}{K_2} = \frac{q(T_2 - T_1)}{R(T_2 \times T_1)} \quad \dots \quad (20),$$

where K_1 and K_2 represent the ionisation constants for water at temperatures T_1 and T_2 . R is the gas constant which equals 1.986 calories per degree, and q is the heat of ionisation of water or 13,700 calories. Inserting these values in Equation 20, $K_w = 0.81 \times 10^{-14}$ at 20° . This value was used for the calculation of the ionisation constants of both methyl-orange and phenolphthalein.

(To be continued).

BRITISH EMPIRE INDUSTRIAL EXHIBITION.

ADVISORY COMMITTEE FORMED.

BRITISH MANUFACTURERS AWAKING AT LAST.

To further the scheme for the holding of a British Empire Industrial Exhibition at the conclusion of the war, which is being organised by the Institute of Industry of Great Britain and Ireland, Ltd., Aldwych Site, Strand, W.C., an Advisory Committee has been formed. The members of this Committee are :—

- Mr. Algernon E. Aspinall, Secretary, West India Committee.
- Sir Herbert H. Bartlett, Bart., Institute of Builders.
- Mr. G. McLaren Brown, the Canadian Pacific Railway.
- Mr. Walter Deakin, the Machine Tool and Engineering Association.
- Mr. Lewis Evans, J.P., President, Papermakers' Association.
- Mr. P. J. Hannon, Secretary, the Navy League.
- Sir James Heath, Bart., British Iron Trade.
- Mr. Andrew Home-Morton, M.I.C.E.
- Hon. John Howard, Agent-General for Nova Scotia.
- Mr. M. T. Kaderbhoy, of Bombay.
- Hon. Sir John McCall, M.D., Agent-General for Tasmania.
- Mr. T. C. Moore, J.P., Staffordshire Potteries' Manufacturers' Association.
- Mr. J. Taylor Peddie, F.S.S., Chairman, Institute of Industry.
- Hon. P. Pelletier, Agent General for Quebec.
- Mr. John A. Reid, Agent-General for Alberta.
- Hon. Richard Reid, Agent General for Ontario.
- Mr. Charles J. Stewart, the Public Trustee.
- Mr. F. W. Sumner, Agent-General for New Brunswick.
- Hon. Sir John Taverner, K.C.M.G.
- Hon. J. H. Turner, Agent-General for British Columbia.
- Mr. Frank Warner, President, the Silk Association of Great Britain and Ireland.

There will be two Exhibitions in reality. The first, an Exhibition of All-British Industries, will run for one month only, and the second, showing the natural resources of the Empire and its industries as a whole, for three months. Both have received influential support, and in the character and dimensions of the buildings and in the scope of its enterprise the Exhibition will excel any effort yet made in this country or by similar organisations in Germany.

The Exhibition of purely British industries will be sectionised somewhat on the following lines :—

- | | |
|------------------------|---------------------------|
| Iron and Steel Trades. | Shipping. |
| Textile Industries. | Shipbuilding. |
| Engineering. | Leather Trades (embracing |
| Electrical Trades. | Boot and Shoe Industry). |
| Silk Industries. | Food Products. |
| Printing Trades. | Clothing, Drapery, and |
| Furniture Trades. | Millinery. |
| Building Trades. | Harbour and Dock Equip- |
| China and Pottery. | ment. |
| Metal Industries. | &c., &c. |

The sectionising of the Exhibition of the Natural Resources and Industries of the Empire would follow on somewhat similar lines.

Need and Value of the Exhibitions.

The need of a British Empire Industrial Exhibition has been demonstrated repeatedly since the war began, and as a nation we have begun to appreciate to a much greater extent than hitherto the material advantages to be derived from the development of the natural resources of our Empire. It has been shown that we have allowed foreign countries, Germany particularly, to control those indus-

tries closely identified with the development of natural materials, such as zinc, lead, spelter, copper, tin, aniline dyes, pharmaceutical products, palm kernel oil, &c.

With a view, however, of enabling the British public to appreciate in full the enormous resources of the Empire in natural materials, and with a view of capturing those industries engaged in the development of these and now largely controlled by Germany, it is proposed to make the Exhibition of British Industries and of the Natural Resources of our Empire in 1917 of as comprehensive a character as possible.

In view of the great services which the Dominions and Colonies have rendered to us in the titanic struggle now progressing, it is our duty to ensure that the British race as a whole shall emerge from this struggle stronger than ever, and with a determination to maintain its national and imperial industries upon the highest possible basis of efficiency. We must never allow Germany to control those industries which are vital to the life of the nation when it fights for its existence. We have seen what German organised industries can do. In the supply of munitions of war Germany has been able to defy the four countries surrounding her, and in the development of natural materials up to the present she has had no competitor of consequence. At the conclusion of the war we may expect strenuous competition from her in all phases of industrial activity; she will be continually knocking at the door of our economic life unless we organise now and take steps to adopt such measures as will neutralise the advantages they now hold.

It is the intention of the Joint Committee to show the particular branches of industry in which the natural resources of our Empire can be most profitably utilised. Particular care will also be exercised by the Committee in showing at the Exhibition the uses which Germany has made of our natural resources in the development of her industries, notably her chemical industries. If it can be arranged it is proposed to give practical demonstrations, which should be helpful in enabling our industrialists to appreciate the benefits to be derived from the application of science to industry, and in indicating in which of our dominions, colonies, or possessions the requisite natural materials can best be obtained.

Openings for Trade.

On the return of peace there will be a great deal of reconstruction and development work required in Northern France, Belgium, Russia, Italy, Servia, and other Balkan States. In addition the war has retarded to a considerable extent the natural developments of the States of South America and China, and if we desire to secure any portion of the business that will be available we should be ready with the Exhibition in order to compete for it. If we organise for the purpose there is not the slightest reason why British goods cannot replace in the countries mentioned those of German manufacture, and in the carrying out of this object such an exhibition as is suggested would be the market to which all the buyers of the Allied and neutral countries could come.

We should bear in mind that the United States of America has for some considerable time been quietly organising her industrial and financial resources with a view of competing energetically for the orders which must be placed to make good the enormous waste of property and material which the war has brought about. It should be our business not only to prosecute the war to a successful conclusion, but to concentrate our energies in establishing the Exhibition upon a successful basis in order to attract the buyers of our Allies and of neutral countries at the moment they are in a position to place their orders.

The Exhibition proposals have received the full approval of most of the representatives of the Dominions and Colonies, who greatly appreciate the potential value of such an exhibition in the development of the resources of the Dominions and Colonies. Promises of support have already

been extended to the movement, and to such an extent that it would be necessary to devote an Exhibition wholly to the natural resources of the Empire and other imperial industries. For instance, not only has Canada generously supplied us with natural materials and foodstuffs, but her various industries have participated to a very large extent in the production of munitions of war and machinery. It is stated that orders to the value of about £5,000,000 have been placed in Canada alone for this class of material. Canada, therefore, is most anxious to have an exhibition of her manufactures, in order to show the capabilities and capacity of the country for manufacture.

German Domination.

It is hoped that the Exhibition will materially help to release imperial trade from that German domination which prevailed during the years preceding the war. Very few realise what it meant, and many do not realise it even now. Owing to that infinite capacity for taking pains, so characteristic of those who control the financial and industrial resources of Germany, the dye industry was lost to this country, and many others. The metal industry in Australia and South Africa and in other parts of our empire were absolutely controlled by German financial and industrial interests. Such has been the peaceful penetration of the German that even in China our textile manufacturers have been, and in many cases are still, represented by German houses.

NOTICES OF BOOKS.

The National Physical Laboratory. Report for the Year 1914-15. Teddington: W. F. Parrott, Printer. 1915.

In spite of the fact that about 25 per cent of the staff of the National Physical Laboratory are now serving with the colours, the Director's report shows that a considerable amount of important research work has been done during the year, and advice and assistance of great value have been afforded to the Admiralty and War Office as well as to various Government Departments, such as the Home Office, the India Office, &c. In the electrical standards division comparisons have been made of mercury resistance tubes made and calibrated at the National Physical Laboratory and others constructed at Tokio, and also Weston cells made at Petrograd have been compared with the laboratory standards; in both cases the agreement is remarkably good. The comparison of standards of inductance has given equally satisfactory results. The research work on the heating of buried cables has made good progress during the year, and the results will shortly be communicated to the Institute of Electrical Engineers. Some interesting work has been done in photometry, dealing with the methods by which the values of the high-efficiency electrical standards have been obtained, and also formulae have been worked out connecting the light emitted per watt with the temperature of the filament for both carbon and tungsten lamps. In the heat division research work has been done on the loss of heat from surfaces at a high temperature, and the scales of the high-range mercury standard thermometers have been subjected to a very thorough and careful examination, while in the meteorology division much work connected with the maintenance of standards has been carried out. The department of metallurgy and metallurgical chemistry, which has been very shorthanded since the outbreak of war, has latterly been unable to do much more than cope with the investigatory test work and other matters of special urgency, but in this respect it has shown considerable activity, while the record of the engineering department also contains descriptions of a number of valuable researches.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxi. No. 11, September 13, 1915.

Decomposition of Potassium Cyanate by Heat.—A. Portevin.—When potassium cyanate is heated to temperatures varying from 700° to 900° a certain amount of potassium cyanide is always produced, the quantity increasing with the temperature within these limits. The known fact of the formation of KOCN by the action of oxygen upon KCN seems to indicate the reversibility of the phenomenon. If the reversible reaction $\text{KOCN} \rightleftharpoons \text{O} + \text{KCN}$ is admitted, the complete study of the equilibrium KOCN, KCN, and O within the above temperature limits would have to be performed by determining the composition of the fused mixture as a function of the temperature and the pressure of the oxygen, for owing to the miscibility of KCN and KOCN in the liquid state the system is bivalent. The formation of K₂N by heating KOCN establishes an analogy between this latter salt and the chlorates, bromates, and iodates of potassium, which give rise to chlorides, bromides, and iodides similarly.

MISCELLANEOUS.

Supply of Colours.—At the present time the question of the supply of colours is one of great interest to the whole community, and at the same time one of the greatest difficulties in the many branches of industry. It will probably be interesting to many of our readers to know that the Society of Dyers and Colourists have from the time the supply was cut off, taken steps to obviate these difficulties in more ways than one. Dr. F. Mollwo Perkin, F.I.C., F.C.S.—son of the late Sir W. H. Perkin, the founder of the Coal Tar Colour Industry—spoke on the "Future Prospects of the British Dye Industry" to the West Riding Section of the Society in the Hall of the Bradford Technical College on Thursday, October 28. Rufus D. Pullar, J.P., F.C.S., President of the Society, presided.

MEETINGS FOR THE WEEK.

- TUESDAY, Nov. 2nd.—Röntgen Society, 8.15. (At the Institution of Electrical Engineers, Victoria Embankment). Presidential Address. Exhibition of New Apparatus.
- WEDNESDAY, 3rd.—Society of Public Analysts, 8. "Formic Acid as a Reagent in Essential Oil Analysis," by W. H. Simmons. "The Melting-point of Salicylic Acid, and a Test for the presence of Parahydroxybenzoic Acid," by H. L. Smith. "The Persistence of Hydrogen Peroxide in Milk," by E. Hinks.
- THURSDAY, 4th.—Royal Society. "A Diagram to facilitate the Study of External Ballistics," by W. E. Dalby. "An Application of the Principle of Dynamical Similarity to Molecular Physics," by W. B. Hardy. "Motion of a Stream of Finite Depth past a Body," by R. Jones. "Deep-sea Water Waves caused by a Local Disturbance on or beneath the Surface," by K. Terazawa. "Consumption of Carbon in the Electric Arc," by W. G. Duffield.
- Chemical, 8.30. "Reactions between the Higher Fatty Acids and Salts of the Lower Fatty Acids," by A. W. Knap and R. V. Wadsworth. "Interaction of Perchloric Acid and Potassium Sulphate as an example of Reversible Change," by W. A. Davis. "A Decomposition of certain Orihoniromandelic Acids," by G. M. and P. Robinson. "Relation between the Chemical Constitution and Colour of Azo-compounds," by A. C. Sircar. "3,5-Dimethylpyridine," by J. G. M. Dunlop. "Compounds of Iron, Manganese, Lead, and the Metals of Group II" and "Valency," by S. U. Pickering. "Indirect Determination of Velocity of Hydrolysis by the Polarimetric Method," by J. C. Crocker. "Vapour-pressures of some Saturated Aqueous Solutions," by M. P. Applebey and W. Hughes.

THE CHEMICAL NEWS

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ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION. MANCHESTER, 1915.

By Prof. W. A. BONE, D.Sc., F.R.S., President of the Section.
(Concluded from p. 217).

FUEL ECONOMY AND THE PROPER UTILISATION OF COAL.

LEAVING now the scientific aspects of flame and combustion, I wish to say a few words as a technologist upon the great national importance of a more adequate scientific control of fuel consumption and the utilisation of coal generally, with special reference to the situation created by this terrible and ruinous European conflict. And my remarks will be addressed in part to my chemical friends and colleagues, who are primarily interested in scientific research and its industrial applications, and in part also to the commercial and manufacturing community which is chiefly interested in the financial results of such scientific activity.

Notwithstanding the fact that we are raising annually in the United Kingdom—according to the official estimate for 1913—287 million tons of coal, of which 189 million tons (or, say, 4 tons per head of the population) were consumed at home, more or less wastefully, it is indeed surprising how little has been done, or is being done, by the scientific community to impress upon the Government and the public generally, the importance of establishing some systematic control or investigation of fuel consumptions in all large industrial areas. Deputations have waited upon the Government about the question of reviving our languishing coal-tar colour industry, so that in future we may be independent of Germany for the supply of the £2,000,000 of dye-stuffs required by our textile industries, and already a State aided organisation, with an advisory scientific committee, has sprung into existence to achieve this desirable result. But no organised body of scientific men, so far as I know, has ever thought it important, or worth while, to take an active interest in the vastly greater subject of fuel economy and the proper utilisation of coal, upon which the dyeing industry depends for its raw material.

It is unnecessary for me to remind you that the contending armies in this Armageddon of the nations depend upon certain distillation products of coal for their supplies of high explosives; and there is little doubt in my mind but that Germany's violation of the neutrality of Belgium, and her subsequent seizure of that country and of a large tract of Northern France, had more than a purely political or strategic significance. She, doubtless, wanted also to seize for herself (and at the same time to deprive her enemies of) coalfields lying just beyond her own borders, which are capable of furnishing abundant supplies of coal admirably adapted for yielding the raw materials for the manufacture of high explosives. A country in which all metallurgical coke has for years past been manufactured under chemical supervision in by-product coking-ovens, with recovery of ammonia, tar, and benzol, and in which the wasteful beehive coking-ovens have long ago ceased to exist, was hardly likely to overlook the military importance of the Belgian coalfield, with its many by-product coking plants. And, moreover, but for German commercial acumen and enterprise, during many years past, our own by-product industry would not have attained even to its present respectable dimensions. Certainly it owes very little to the interest or attentions of British chemists, most

of whom are, unfortunately, but little aware of its circumstances and conditions, and seem to care even less for its particular problems. And yet, in proportion to the capital outlaid upon it, it is one of the most profitable of all our chemical industries, coal-tar colours not excepted.

Fuel economy, and the proper utilisation of coal, whether in connection with manufacturing operations or domestic heating, will become one of the most important national questions during the trying years that will follow hard upon this war, because of all directions in which national economy can be most healthfully and advantageously exercised, this is perhaps the most obvious and prolific. For it is tolerably certain that, with an efficient and systematic public supervision of fuel consumptions, we ought to be able, even with existing appliances, to save many millions of pounds of our annual coal bill, and with improved appliances still more millions—a saving which would in the long run redeem a considerable amount of the war loan which has been much more easily raised than it will be repaid.

Now, I fear that not only are chemists for the most part lamentably ignorant of the nature of coal, and of modern fuel technology, but they have been for many years past so indifferent about such questions that they have been content to leave them almost entirely to engineers who, as a body, are notoriously deficient in chemical sense and experience. The engineer has indeed not usurped the place of the chemist, but has had to do his best to fill the position long since abdicated by the chemist.

This, indeed, seems strange when we remember that the foundations of modern chemistry were deeply laid by investigators who were, above all things, "fire worshippers." But, judging from most chemical text-books, nearly all that the modern student of chemistry is taught in our academies about combustion was known to Lavoisier; and I question whether in the majority of our university laboratories any investigation on coal or combustion is ever undertaken. And yet the subject is full of most fascinating and fundamental theoretical problems—for the most part unsolved—and the nation consumes every week as much coal as could be exchanged for the whole quantity of aniline dyes used by its textile industries in a year.

Moreover, such advances as have been made during recent years, and they are by no means inconsiderable, have nearly all been in the direction of the wider applications of gaseous fuels. Yet in how many of our university laboratories is even gas analysis taught, or how many of our schools of chemistry provide systematic courses in the chemistry and manipulation of gases, without which no professional training of industrial chemists, however much "research work" it may include, ought to be considered satisfactory? It is my opinion that this important branch of our chemical craft and science has not, for many years past, been accorded its proper place and share of attention in the ordinary curriculum of the majority of our academic institutions.

Of the 189 million tons of coal consumed in the United Kingdom in the year 1913, about 40 million tons, or (say) approximately one-fifth of the whole, were carbonised either in gasworks, primarily for the manufacture of town's gas, or in coke-ovens for the manufacture of metallurgical coke in practically equal proportions. Two-thirds of the latter was carbonised in by-product recovery plants; the remainder in the old wasteful beehive ovens. So that, roughly speaking, we have—

Total coal carbonised = 40 million tons.		
In gas works.	In by-product coke-ovens.	In beehive coke-ovens.
20	13.5	6.5

At present there are 8297 by-product coke-ovens built in this country of which 6678 are fitted with benzol recovery arrangements, capable of producing something like 10 million tons of coke per annum.

The yields of the various by-products obtainable on such coke-oven installations naturally vary with the locality and character of the coal seam; but they probably average somewhat as follows—expressed as percentages on dry coal carbonised:—

District.	Ammonium sulphate.	Tar.	Benzol and toluol as finished products.
Durham	0.9 to 1.45	2.5 to 4.5	0.6 to 1.0
Yorkshire	1.3 " 1.5	3.5 " 5.0	0.9 " 1.1
Derbyshire	1.3 " 1.6	3.5 " 5.0	0.9 " 1.1
Scotland	1.4 " 1.6	3.5 " 5.0	0.9 " 1.1
South Wales	0.9 " 1.1	2.0 " 3.5	0.6 " 0.75

Or, to put the matter a little differently, each ton of dry coal carbonised yields from 20 to 35 lbs. of ammonium sulphate, from 56 to 112 lbs. of tar, and from 2 to 3½ gallons of crude benzol, &c.—according to the locality. About 65 to 70 per cent of the crude benzol is obtained as finished products—benzene, toluene, solvent and heavy naphthas.

How rapid has been the development of the by-product coking industry in this country during recent years may be judged from the following official returns of the quantities of ammonium sulphate annually made by such plants, as compared with the corresponding quantities produced in gasworks.

Tons of Ammonium Sulphate Produced in—

Year.	By-product coke oven plants.	Gas-works.
1903	17,435	149,489
1908	64,227	165,218
1913	133,816	182,180

In the natural course of events, the final disappearance of the wasteful beehive coking-oven from this country is now only a matter of a few years; but I venture to suggest that public interest would justify the Government fixing, by law, a reasonable time-limit beyond which no beehive coke-oven would be allowed to remain in operation, except by expressed sanction of the State, and then only on special circumstances being proved.

There is also much need of a better and more systematic chemical control, in the public interest, of by-product coking plants. At present, in far too many cases, the chemists employed in coke-oven laboratories are men who have practically no chemical training other than that obtained in evening classes. And, with few exceptions, the chemist, however competent he may be, is entirely subordinated to the directing engineer, and regarded as a mere routine analyst. I can say, from personal knowledge, that plants which are managed and controlled by experienced chemists of broad training, combined with force of character, yield much better results than those which are controlled by men without such qualifications.

And even in this crisis when so much depends on plants working not only at their maximum output capacities but also, chemically speaking, under conditions calculated to ensure the highest yields of benzol and toluol, with a proper selection of coal, I doubt whether the measures which have been taken to advise and supervise the coke-oven industry are really adequate from the point of view of chemical control. I do know, for instance, that the experience and resources of the majority of our University Departments of Applied Chemistry which specialise on fuel technology and cognate matters have not been as fully utilised as they might have been in this connection. I cannot for one moment imagine a similar state of things being permitted in Germany, where we may be sure that nothing is being left undone in the way of fully utilising all the available expert chemical and engineering knowledge which can be brought to bear on this important aspect of war munitions, and I venture to say that, whatever may be the case in this country, in Germany at least the staff and resources of no publicly maintained Department of Fuel Technology will not be fully employed on war problems.

The coal-gas industry, which deals with some 20 million tons of coal per annum, has, especially within recent years, shown a growing appreciation of the aid of chemical science, in regard not only to the actual manufacture but also to the domestic and industrial uses of coal-gas. The endowment by the industry, in 1910, of a Special Chair at the Leeds University, in memory of the late Sir George Livesey (of which I had the honour and pleasure of being the first occupant) was a sure sign of the faith of its leaders in the value of scientific research into its special problems, and, from personal knowledge and intercourse with gas engineers, I can assure my chemical colleagues that any serious interest taken by scientific chemists in these problems, or in training men to tackle them, will be welcome by the industry, no matter from what quarter such help or interest may come. For although the carbonisation of coal in gas-works is efficiently carried out, no one in the industry supposes that finality has been reached, or that existing methods and conditions cannot be improved under better chemical control.

And, moreover, the gas industry has just recently given a striking example of the public benefit which may accrue from the whole-hearted co-operation of the chemist and engineer in the new nickel-catalytic process for the removal of carbon bisulphide from coal-gas, which has been worked out, and brought to a successful issue, by the combined skill and efforts of Mr. Charles Carpenter, D.Sc., Mr. W. Doig Gibbs, and Mr. E. V. Evans, of the South Metropolitan Gas Company. They have shown that the sulphur content (as CS₂) of London coal-gas can be reduced on a large scale, in regular day to day working, from nearly 40 to about 8 grains per 100 cubic feet, without in any way deteriorating the quality of the gas, at a cost (including interest and depreciation) of 0.299 d. per 1000 cubic feet. Such a striking success was, as Mr. Carpenter acknowledges, only achieved "because of the unrestricted and unreserved collaboration of the chemist and the engineer." Incidentally, the gas industry is to be congratulated on this tacit abandonment of the old contention that coal-gas was either none the worse for the presence in it of a certain amount of sulphur compound or (alternatively), if worse, that a minute amount of sulphur dioxide in the atmosphere of a living room is so rapidly absorbed by the ceiling that its harmful effects are nullified.

As the outcome largely of the work of the Joint Committee appointed in 1907 by the Institution of Gas Engineers and the University of Leeds (of which I was a member) to investigate gas-fire problems, the manufacturers of these appliances have paid much more attention than formerly to the scientific aspects of construction, so far as to ensure the best combination of radiant and ventilating effects, and nearly all the larger firms have now their scientific staffs busily employed in making further advances. Prominent among the pioneers in scientific gas-fire construction has been Mr. H. James Yates, who will enlighten you as to some of the most recent improvements. I can, however, from personal knowledge, testify to the enterprise shown by most of the leading manufacturers, and that their combined efforts have resulted in a very efficient and perfectly hygienic domestic gas-fire. A Committee appointed by the Institution of Gas Engineers, upon which scientific men are largely represented, is now considering the adoption of a standard method of testing the radiant efficiencies of gas-fires. Thus no one can say that the gas industry is not making every effort to put its affairs upon a thoroughly scientific basis.

Passing on to the metallurgical and allied industries (who, of course, are large consumers of fuel), there is much here to be done in improving the construction and operation of furnaces in order to check the waste of fuel. But of these details there is no time to treat, and one instance of the possibilities of very large economies as the result of scientific control must suffice.

It is perhaps common knowledge that the most economical arrangement of plant for the manufacture of

iron and steel is one in which by-product coke-ovens, blast-furnaces, steel furnaces, and rolling mills are brought together on one site and under one organising direction, so that the surplus gases from the coke-ovens and blast-furnaces may be utilised to the fullest extent. My relative, Mr. T. C. Hutchinson, of the Skinninggrove Iron Company, who has devoted many years of anxious thought and practical study to this important problem, ventured some few years ago to predict that—with the most approved type and arrangement of plant, working under strict scientific control by competent chemists—it would soon be possible to make finished steel rails or girders from Cleveland ironstone with no further consumption of coal than is charged into the by-product coke-ovens for the production of the coke required for the blast-furnace, and all subsequent experience at Skinninggrove has fully demonstrated that his prophecy can be fulfilled in everyday practice. Of course, it means a constant watchful control by a well-paid and competent scientific staff under efficient leadership, and in Mr. E. Bury—an old Owens College student, trained in an atmosphere of "gas and combustion"—we have found the very man for the work.

It is perhaps unnecessary, even had time permitted, for me to multiply instances of possible economies in other important directions—such, for instance, as power production and the heating of domestic apartments. There is probably no direction in which equally good results would not accrue with proper scientific application and control as those already cited as having been reached in the direction of carbonisation, or in the iron and steel industry. We are to discuss the important subject of smoke prevention, in which many Manchester public men are showing an active interest; so that there will be some further opportunity of referring to the matter.

But may I, in conclusion, appeal in all seriousness to chemists and scientific men generally to take up this important matter effectively as a public duty at this crisis in the country's affairs. I would suggest that the Government be memorialised with a view to the establishment of a central organisation for the supervision of fuel consumption and the utilisation of coal somewhat on the lines of the existing alkali works inspection, which has been so beneficial to chemical industry. And in connection with such an organisation there might be undertaken a much-needed systematic chemical survey of British coalfields, as well as experimental trial of new inventions for fuel economies. There would certainly be no lack of important work for such a properly-organised department of the State, and there can be no doubt at all that the results of its activities would be not only a very large direct saving in our colossal annual coal bill, but also a purer atmosphere and healthier conditions generally in all our large industrial areas.

THE LENGTH OF THE FIBRE OF THE SOUTHERN PINE.

By CLAYTON BEADLE and HENRY P. STEVENS.

IN 1912 we examined fifty-five papers produced from different kinds of United States pulp woods supplied to us by the Forest Service of the United States Department of Agriculture. These pulps were produced from woods hitherto unused in the manufacture of paper. Among other things we determined the length of fibre, taking between 600 and 700 readings. The results of these determinations were published in the *Paper Maker* (1912-13, p. 155), in tabular form, with a final table giving the different pulps from the different shipments, arranged in order of length of fibre. The pulp which gave the longest fibre was that produced from the Longleaf Pine. This gave the highest readings we have ever noted for a pulp wood. The Longleaf Pine (*Pinus palustris*, Mill) ranges from Southern Virginia (Norfolk) to Florida (Tampa Bay and Cape

Canaveral) to Eastern Texas (Trinity River); northward in Alabama to the north-eastern part of the State (Clay and Walker counties), and North-western (border counties Georgia. It is also commonly known as the Southern Pine, and by no less than twenty-four other names in the various regions of the United States, but it is generally referred to in paper-making circles as the Southern Pine.

The very strongest sulphite pulp that has ever entered this market was when examined found to have a length of fibre the mean figures of which vary according to make from about 3.08 mm. to 3.42 mm. The average lengths of strong pulps, however, is about 2.5 mm. The length of fibres found in strong kraft papers, produced from wood pulp, is about 2.5 mm. The Longleaf Pine is interesting because the shipment examined and converted into pulp and paper by the United States Government, according to our figure, showed 4.28 mm. as the average length. It heads the list with White Fir, coming next with 4.02 mm., and Douglas Fir, 3.32 mm.

Some large lumbering concerns on the St. John River, near Jacksonville, Florida, have discovered that their waste from the Longleaf Pine can be converted into pulp possessing an exceptionally long fibre, and that 1.7 cords of wood would be sufficient for the production of one ton of bleached pulp. We have received a sample of this pulp and have determined the length of fibre, the results of which are contained in the following table:—

Field 1.	Field 2.
mm.	mm.
6.62	4.32
3.92	5.30
4.54	5.10
6.42	4.36
3.88	5.14
4.38	4.54
5.52	4.24
7.12	5.36
6.08	6.38
5.78	6.56
Mean of each set of ten..	5.426 5.130
Mean of all	5.278

This shows a mean length of 5.278 mm. This is significant in being double the length of the fibre that is found in strong pulp in kraft papers such as are used for the manufacture of paper yarn. We have repeatedly shown that the utility of paper yarn is in a large measure determined by the length of the ultimate fibre of which the paper is composed. The greater the length of the fibre the nearer will the strength and other qualities of paper yarn approach to ordinary yarns.

Now the limit of economic handling in the textile industry is reached with a length of fibre from 3—5 mm., a length which is never reached with present-day papers made from wood pulp, even with the strongest kraft papers. If, however, a source of supply of wood pulp is available, having an average length of something over 5 mm., provided that it meets with all other necessary qualifications, the paper-yarn industry is likely to derive great benefit, and the uses of paper yarn will be considerably extended beyond their present limits. It will be noted, from an examination of the individual figures in the above table, that there is not much variation in the staple. The lowest figure is 3.88 mm. and the highest figure 7.12 mm. This points to considerable uniformity of length. We think these readings mark the Longleaf or Southern Pine as providing the longest fibre ever recorded for the manufacture of wood pulp and paper.

Mr. G. D. Wells, of the Forest Products Laboratories, Madison, Wisconsin, has recently issued some interesting details, and refers to the Longleaf pine as having a figure averaging from 3½—4 mm., and capable of producing a kraft paper of high strength and resistance to wear. He also states that the chips can be reduced to

pulp with a very short cooking period, and that a high yield of pulp per cord is obtained. The papers we have seen produced from this wood show a very long tear. The figures given in the above table show that in certain localities at any rate the Southern pine yields a length of fibre which is very much in excess of the specimens examined by the United States Government Laboratories, and that such wood is worth selection for the purposes above enumerated.

INTRODUCTION TO THE THEORY OF RELATIVITY.

By F. H. LORING.

THE principle of relativity represents one of the most remarkable and revolutionary ideas the scientific world has had to consider. Whether the relativity concepts in their entirety will stand the test of time is doubtful, but it is of importance to try and get some idea of the theory, since the principle involved, under some further development or elucidation, may come into universal favour.

The following is an attempt to explain this theory in a simplified way, or, rather, to state the matter so as to give the student something to stimulate further inquiry into this fascinating but complicated subject.

This theory, or the modern relativity as it has been termed, is the invention of Einstein. To Minkowski, however, is due the credit of having strengthened the theory by a rigorous mathematical treatment, which makes it possible to pass from a stationary to a moving system of co-ordinates, the transformation retaining Maxwell's equations.

The theory apparently arose from the difficulty of reconciling certain optical phenomena with each other, or with the theory of an æther, especially when the electromagnetic-wave theory of light is taken into account; and so far as it brings about the interpretation of the phenomena by accepting certain postulates, it is certainly a unique achievement. The mathematical methods involved, or in general the introduction of certain constants in applying the theory, may be open to objection, but these are matters for mathematicians and electricians to thrash out.

It will be necessary first to become familiar with the phenomena in question. It was discovered long ago that the light rays from a fixed star on entering the lens-system of a telescope were displaced from the true central or optical axis of the instrument by such an amount as would result if the telescope were considered as moving in space across the path of the rays, that is to say, moving with the earth. In reality, however, the telescope has to be pointed slightly away from the star to get the focal image on the cross-hairs of the eye-piece of the instrument, and this must be taken into consideration. It is simple to understand, since the light propagation has a definite known velocity, and the earth carrying the instrument is in sideways movement relative to the light rays from the star. It is as if one wanted to pocket a ball in a cup centrally situated at the bottom of a long tube without the ball ricocheting along the wall of the tube while the tube was being bodily moved in a direction at right angles to the line joining the thrower of the ball to the holder of the tube. It is evident that the tube must be angularly turned out of this line to pass the ball comfortably to the pocket. In other words, the telescope has to be pointed a little away from the star to catch the rays of light centrally. This phenomenon is known as the **aberration of light**.

Since accurate observations extending over a year are required to detect this phenomenon, it is desirable to state the above in the following way (an expeditious method has been recently proposed, but this need not be discussed here). At different times of the year the telescope has to be pointed in a slightly different direction to keep the star-image on the cross-hairs of the instrument, and, by

studying closely this change in angular position from time to time, it has been found that the altered adjustment has not to be made owing to the movement of the star, the star being from our point of view a fixed one, but owing to the movement of the earth across the path of the rays, as distinguished from any movement in a direction along the rays. Very careful examination has led to the conclusion that, owing to the passage of the rays (light propagation) down the telescope tube at a certain known velocity, while the tube itself is under known transverse movement, the tube is really pointed or sighted a little in advance of the star to keep the rays to the true optical axis. The adjustment of the tube being angular, the angle thus obtained is termed the **angle of aberration**, which can be calculated from the velocity of light and the velocity of the instrument in space, that is to say, in its orbital motion with the earth round the sun.

"The angle of aberration being determined by the ratio of the earth's velocity to the velocity of light,* we should expect a change if either one of those quantities could be altered." Inasmuch as the velocity of light in a dense medium like water is less than in air, it was expected that the filling of the telescope tube with water ([Boscovich]-Airy experiment) would alter perceptibly the angle of aberration, i.e., it would be increased. No difference was found, however, upon making the experiment. This negative result was predicted by Fresnel, who took into account an æther effect. The part played by the supposed æther contained in or associated with ponderable matter has to be considered.

It was suggested that the æther in the water was dragged along, this drag being sufficient in magnitude to account for the negative result in the foregoing experiment. This so-called drag then might just compensate for the slower propagation of the light through the substance, the æther moving "sideways" with the matter to some extent—or some of it (that in excess of the amount which would fill the space if the water were removed) moving to a complete extent—and, moreover, this compensative effect if of the right or "half"-magnitude would be in conformity with Maxwell's equations for electromagnetic-wave propagation; but experiments on different moving media give variable values (coefficients) that are in each case proportionate to the refractive index of the substance, and this does not seem to fit in with Maxwell's equations.

The fringe-displacements in certain experiments (see below) are proportional to the velocity of the moving medium, and in changing from one substance to another the displacement in each case can be calculated from the *dragging coefficient* (*coefficient d'entraînement*) and the corresponding *velocity* of the medium, the former being a function of the refractive index.

Arago, in the year 1818, it would appear, suggested that a prism, moving along the line of the rays, should bend the light to a greater or less extent according to the velocity and direction of its motion, since he evidently thought that the "velocity" of the ray in traversing the distance *a* (or meeting the prism) would be altered relatively to that of *b* (see Fig. 1, in which $w = w =$ wave-fronts), but Fresnel pointed out in effect that the velocities would be proportional in both cases, or the new times equal, since the light disturbance passes through the glass of the prism at a proportionately altered velocity (relative, of course, to that of the glass itself), and this agrees with Arago's experiment, which gave a negative result. With water, in the Fizeau experiment, the dragging coefficient is 0.434, with an error of ± 0.02 . This is practically a half-value.

Fizeau's experiment consisted in projecting two beams of light through a U-tube arrangement, through which water was circulated at a velocity of seven metres per second, and in such a way as to get interference fringes at the union of the two beams.

* This ratio, by the way, is often termed the *aberration constant*.

Michelson and Morley confirmed the result with an improved type of apparatus, the optical scheme of which is shown by Fig. 2 (the tubes in this apparatus were six metres long), and they found by reversing the direction of flow that a displacement of less than the width of a single fringe was observed. The coefficient of drag above given is the value these experimenters obtained.

If we are going to draw any conclusion from the dragging effect we must consider the *æther* as "part and parcel" of nonderable matter which leaves the *æther* proper as a stationary medium, that is to say, if we interpret the dragging experiments in the Fresnel sense. This really amounts to a sort of negative interpretation, because the next step would be to do away with the *æther* entirely, for, how could it be stationary with respect to

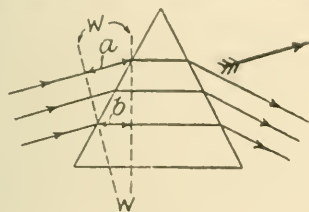


FIG. 1.

one thing and not another? In this connection I will re-state in practically Dr. Silberstein's words a passage from his "Theory of Relativity," 1914, p. 42 (Macmillan):—Lorentz's theory, now widely known as the Electron Theory, is, first of all, based upon the assumption of a stationary, isotropic, and homogeneous *æther*. In calling it in short 'stationary' (stagnant), Lorentz states expressly, that to speak of the *æther's* 'absolute rest' would be nonsense; that what he means is only that the several parts of the *æther* do not move relatively to one another. In other words, Lorentz's *æther* is not deformed, it is not subjected to strain, and consequently it does not execute any mechanical oscillations; this being the case, it has, of course, no kind of elasticity, nor inertia, nor density. It is thus far less corporeal than

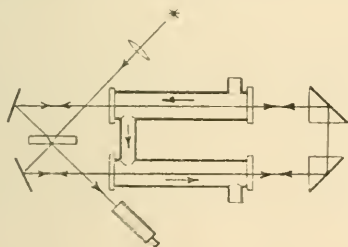


FIG. 2.

Fresnel's *æther*. In fact, one fails to see what properties it still has left other than that of being a colourless seat (we cannot even say *substratum*) of the electromagnetic vectors E , M . Although Lorentz himself continues to tell us, in 1909, in his "Theory of Electrons," that he 'cannot but regard the *æther* as endowed with a certain degree of substantiality,' yet, for the use he ever made of the *æther*, he might as well have called it an empty theatre of E , M , and their performances; or, a purely geometrical system of reference, stationary with regard to the 'fixed' stars, or at least to some of them. This *æther* having been deprived of its properties was therefore so nearly non-substantial that the first blow it had to sustain from modern research knocked it out of existence altogether—as will be seen later. Still, substantial or not, for the purpose of the theory of Lorentz which we are now con-

sidering, it is *something*, namely, a unique system of reference. So long, therefore, as it was thought that there is such an unique system Lorentz's all-pervading medium could continue its scanty existence.*

(To be continued).

THE ELECTROLYSIS OF NITRIC, SULPHURIC, AND ORTHOPHOSPHORIC ACIDS USING A GOLD ANODE.†

By F. H. JEFFERY, M.A.

SOME of the effects of using a gold anode in certain cases of electrolysis are described in the course of a paper by Lenher (*Journ. Am. Chem. Soc.*, 1904, xxvi., 550); for solutions of sulphuric acid and of potassium sulphate a more detailed account is given by Mixer (*Ibid.*, 1911, xxxiii., 688). In the following investigation further details are given of the reactions taking place with a gold anode. The cell used was formed of a Jena beaker of 800 cc. capacity, inside which was a porous pot. The volume of the anolyte was about 550 cc. The gold anode hung from a platinum wire in the beaker, the platinum being above the surface of the electrolyte. The platinum cathode was placed inside the porous pot. A glass stirrer turned by means of a motor revolved in the beaker close to the anode. The beaker and its contents were placed in a large vessel of cold water.

In all cases the solid gold compounds were formed quite homogeneous in appearance, and the analyses of samples obtained under the same conditions were consistent with this. The weight of gold entering into combination per faraday was small, being not greater than 2.5 grms. in any of the following experiments:—

Nitric Acid Electrolyte.

(i.). The concentration of acid used was that corresponding to 100 cc. HNO_3 of density 1.42 diluted with 100 cc. water. The temperature 12°C . to 16°C .

At first experiments were made without a porous pot around the cathode.

A current of 4 amperes was used.

On closing the circuit much hydrogen was evolved at the cathode, and the difference of potentials of cathode and anode was 4.4 volts. After about one minute the voltage fell to 3.7 volts, and hardly any gas was evolved at the cathode.

The current and voltage remained constant after the initial fall of voltage during several hours.

The electrolyte became of a pale yellowish green colour, the cathode was covered with a brown solid, and the same brown solid was distributed throughout the electrolyte.

This solid was analysed. On heating it gave Au and H_2O only. It was dried for three hours over concentrated H_2SO_4 in a vacuum desiccator, and gave 99.9 per cent Au (0.3921 gm. taken).

Au was precipitated from the green electrolyte by SO_2 and by HNO_2 .

It appears therefore that gold is dissolved from the anode, forming a green compound, which is reduced to metallic gold by the hydrogen dissolved in the platinum cathode.

A series of experiments were made using a porous pot around the cathode.

The acid used for the catholyte was of the same concentration as that used for anolyte. Various currents and current densities were employed.

The anode decreased in weight. During the solution of the gold no deposit was formed on it, neither was there finely-divided gold distributed through the anolyte.

* The purport of this quotation does not, of course, represent a universally-accepted view.—F. H. L.

† A Paper read before the Faraday Society, October 19, 1915.

* This is perhaps mere words.

The cathode remained bright and entirely free from any deposit of gold. The acid in the pot was reduced to nitrous acid, nitric peroxide being evolved; also no gold was found on the inner surface of the pot.

The anode acid became a deep olive-green colour owing to the gold compound formed. As the electrolysis proceeded, the colour changed to a bright sherry hue, and finally to a deep yellow-brown. Gold was at once precipitated from the anolyte by HNO_2 and by SO_2 .

It appears therefore that the gold goes into solution as complex anions. The colour changes may be due to changes in the relative proportions of the complex anions and the undissociated compounds to which they correspond, since dilution of the brown-yellow liquid with nitric acid of the same concentration as used originally for the anolyte reproduces the olive-green coloration.

The anolyte, whether at the green stage or later, when kept in a closed flask, deposited a fine black powder on the bottom of the flask. This was found to be pure gold.

Bright yellow metallic scales were formed on the surface of the liquid; these were also gold.

A weighed strip of gold was left in the anolyte for about sixteen to seventeen hours, and then re-weighed. No gold was dissolved. (Temperature about 15°C .) Some of the yellow-brown anolyte was kept at -16°C . for about five hours. No crystals were obtained. Hardly any of the fine black gold described above was formed.

Some of the same brown-yellow anolyte was placed in a vacuum desiccator over concentrated H_2SO_4 with a vessel containing sticks of NaOH close to it. The HNO_3 distilled and metallic gold separated from the solution, and finally small lemon-yellow crystals were formed. These had the appearance of auri-nitric acid, $\text{HAu}(\text{NO}_3)_4 \cdot 3\text{H}_2\text{O}$.

These were analysed by adding to a known weight of the crystals a known volume of water. Nitric acid was formed in solution, and the orange-yellow insoluble solid formed at the same time was ignited and the gold obtained weighed. The percentage of gold in the crystals was found to be (a) 39.52, (b) 39.22, giving a mean 39.37.

The nitric acid was titrated with KHCO_3 solution, and the value of NO_3/Au was found to be (a) 3.95, (b) 4.08, giving a mean 4.01.

A small quantity of the orange-yellow solid was analysed for the gold to oxygen ratio by heating it and collecting the oxygen. This was found to be 8.26. The crystals were very hygroscopic, and appeared to be partially hydrolysed in contact with air containing water-vapour.

For auri-nitric acid crystals the calculated percentage of gold is 39.42, the value of NO_3/Au is 4.00, and for hydrated Au_2O_3 the gold to oxygen ratio is 8.22.

It appears therefore that the crystals are auri-nitric acid.

Some of the yellow-brown anolyte was added to a large volume of cold water (temperature about 12°C .) An orange-yellow precipitate was obtained. This was washed and left under water for three weeks, the water being changed frequently. Finally, the washings gave no acid reaction with litmus and no precipitate with nitron (diphenyl-endo anilo-dihydro-triazole).

The powder was dried for ninety hours over concentrated H_2SO_4 in a vacuum desiccator.

When heated, oxygen and gold were formed and water evolved, which was acid to litmus, and contained a small quantity of nitric acid.

The proportion by weight of gold to oxygen = 8.34; for hydrated Au_2O_3 this proportion = 8.22.

The powder was completely soluble in cold dilute HCl .

The anolyte was electrolysed, using a platinum anode, and a platinum cathode surrounded by a porous pot containing nitric acid diluted with its own volume of water. There was no deposition of gold on either electrode; the gold compounds in the anolyte did not appear to be affected by the passage of the current.

The quantity of gold dissolved per faraday of electricity was 0.0104 grm.-atom ($\text{Au} = 197.2$) for a current of 1 ampère and anode area $2 \times 4.61 \text{ cm}^2$, the number given

being the mean of ten determinations made when the anolyte was in the yellow-brown stage.

When the current was changed to 0.5 ampère, the anode area remaining the same, the mean of five determinations gave 0.0113 grm.-atom per faraday. (The quantity of electricity was measured by placing a water voltmeter in circuit and collecting the hydrogen evolved in an Ostwald gas burette).

It appears possible that the gold is dissolved partly in the trivalent state and partly in the monovalent state. The anion corresponding to the former appears to be derived from $\text{HAu}(\text{NO}_3)_4$, and to the latter possibly from $\text{HAu}(\text{NO}_3)_2$; the auri-nitric acid has been isolated, but the corresponding aurous compound is hypothetical.

When the anolyte is added to water hydrolysis takes place, and possibly a mixture of hydrated auric oxide and of Au_2O is formed, which would account for the high gold to oxygen ratio. This ratio corresponds to $\text{Au}_2\text{O} \cdot \text{Au}_2\text{O}_3 = 0.02$. The difficulty of washing the product of hydrolysis free from HNO_2 may be due to the formation of a basic auric nitrate which is slowly decomposed in water.

The formation of the fine black gold when the anolyte is kept may be due to the gradual transformation of the aurous compound to the auric compound and gold. At -16°C . such a reaction would proceed more slowly.

(ii.) An electrolyte was used of concentration corresponding to 100 cc. HNO_3 , density 1.42, diluted with 200 cc. water. The anolyte became first olive-green and then yellow. At this stage a red-brown powder separated and was formed in increasing quantity as the electrolysis proceeded. There was no deposit adhering to the anode, and no trace of gold on the cathode.

With a current of 1 ampère and anode area $2 \times 7.10 \text{ cm}^2$, 0.0118 grm.-atom of gold went into combination per faraday. When the powder had settled the yellow anolyte was poured off.

The brown powder was washed with water until the washings gave no acid reaction with litmus, nor any precipitate with nitron.

When heated alone gold and oxygen were formed, and also water, which was only very faintly acid to litmus.

The gold to oxygen ratio was determined by heating the solid and collecting the oxygen. This was found to be (a) 8.61, (b) 8.66, giving a mean 8.63—for Au_2O_3 the value is 8.22. The powder was completely soluble in cold dilute HCl .

Some of the same powder was left under KOH solution at room temperature. The greater portion dissolved. The yellow solution formed was poured off and fresh KOH solution added, the process being repeated during five weeks until the solution poured off ceased to contain any gold compound.

A small residue of violet-black powder remained.

This was washed with water and then dilute HCl was added to it. HAuCl_4 was formed and also a residue of gold.

It appears, therefore, that the brown powder is a mixture of hydrated Au_2O_3 , which is dissolved by the KOH , and of Au_2O . The ratio of gold to oxygen corresponds to $\text{Au}_2\text{O} \cdot \text{Au}_2\text{O}_3 = 0.07$.

The yellow anolyte was poured into a large volume of water at about 14°C , and the product of hydrolysis washed and examined for the gold to oxygen ratio. This was found to be 9.26—considerably higher than that obtained for the brown powder described above.

The water evolved on heating was faintly acid to litmus.

These results seem also consistent with the hypothesis that a mixture of aurous and auric compounds is formed during the electrolysis.

(iii.) A nitric acid of smaller concentration was then used—100 cc. acid to 400 cc. water. The current was 1 ampère and the anode area was $9.80 \times 2 \text{ cm}^2$. Temperature 14°C . The fraction of the gold entering into combination which formed soluble compounds was small, the anolyte becoming a very pale green. A brown magenta

solid was formed at the anode, adhering to it to a small extent.

This was washed and dried as previously described. When the solid was heated, gold, oxygen, and water were formed; the water was very faintly acid to litmus.

The mean value of the gold to oxygen ratio was 8.48—(a) 8.46, (b) 8.51.

The solid was completely soluble in cold dilute HCl. The number of grm.-atoms of gold going into combination per faraday was 0.0114. A portion was placed in cold KOH solution. The greater part dissolved, and when finally the KOH solution left on the solid dissolved no more gold compound, there was a blackish residue, which as in the previous case was found to be Au_2O .

It appears therefore that the brown solid is a mixture of hydrated Au_2O_3 , which is dissolved by the KOH, and of Au_2O . The ratio of gold to oxygen corresponds to $\text{Au}_2\text{O} \cdot \text{Au}_2\text{O}_3 = 0.05$.

The brown solid was soluble in cold nitric acid of concentration used for (i.), giving a greenish yellow solution. This solution gradually deposited finely-divided gold when kept in a closed flask. Its appearance and reactions were similar to those of the yellow-green anolyte obtained from the nitric acid of concentration used in (i.). It was placed in a vacuum desiccator over concentrated H_2SO_4 with a dish containing sticks of NaOH close to it. When it had ceased to deposit gold, the clear solution was decanted, and the nitric acid was allowed to distil until yellow crystals were obtained. These were analysed in the same way as described in (i.). With water they reacted, giving hydrated auric oxide and nitric acid. The percentage of gold in the crystals was found to be 39.21 and the ratio NO_3/Au to be 4.03. For auri-nitric acid, $\text{HAu}(\text{NO}_3)_4 \cdot 3\text{H}_2\text{O}$, the corresponding numbers are 39.42 and 4.00. The crystals are therefore auri-nitric acid.

This result affords further evidence that the gold compounds in solution in the anolyte (i.) are derived from aurous and from auric gold. The proportions of the two compounds are, however, not the same in the anolyte (i.) as they are in the solution just described.

(iv.). A still more dilute nitric acid was used as anolyte, formed from 1 cc. $\text{HNO}_3 \Delta 1.42$ and 10 cc. water.

Acid of the same concentration was used for catholyte.

The current used was 0.5 ampère and the anode area $2 \times 12.9 \text{ cm}^2$.

Care was taken to stop the electrolysis before all the catholyte was reduced to NH_4NO_3 and also before more NH_4NO_3 had accumulated in the anolyte than would give a yellow coloration when 5 cc. of Nessler's solution was added to 10 cc. of the anolyte neutralised with KOH, and made up to 50 cc. with water. (Undissociated NH_4NO_3 slowly diffused through the pot into the anolyte). With these precautions the brown solid formed at the anode was not explosive when heated.

No gold was deposited on the cathode, nor was there any trace of gold compound in the catholyte.

The anolyte contained sufficient soluble gold compound to give a purple coloration when SO_2 was passed into it. The brown solid was washed free from HNO_3 , as in previous experiments, and dried *in vacuo* over concentrated H_2SO_4 . On heating it, gold, oxygen, and water were formed.

No NO_2 was evolved, but the water evolved was acid to litmus. The solid was analysed by heating it and collecting oxygen.

Analyses of two preparations gave the gold to oxygen ratio (a) 8.21, (b) 8.20.

It appears, therefore, that under these conditions hydrated auric oxide is formed, and that such of the gold as forms a soluble compound goes into solution as complex anions only. These probably correspond to $\text{HAu}(\text{NO}_3)_4$, as this compound is formed from Au_2O_3 and nitric acid. The acidity of the water evolved on heating the oxide is probably due to a small trace of a basic nitrate not hydrolysed during the process of washing.

Another experiment was made with an anolyte of this

concentration, using the same anode area but a current of 1 ampère. The results were exactly similar to those described for a current of 0.5 ampère. Analysis of the anode solid gave (a) 8.25, (b) 8.24 for the gold to oxygen ratio.

This appears to be a fairly good method of preparing hydrated auric oxide, the only impurity present being a trace of combined nitric acid; it was found that by stirring the brown solid under water for some weeks and frequently changing the water the nitric acid present could be reduced to so small a quantity that the water evolved on heating the dry solid was only faintly acid to litmus.

The disadvantage of the method is that the hydrated auric oxide is formed slowly; under the conditions used only from 0.04 to 0.05 grm. of gold go into combination per ampère hour.

(v.). An acid of concentration corresponding to 1 cc. $\text{HNO}_3 \Delta 1.42$ to 20 cc. of water was used as anolyte. The catholyte acid was of twice this concentration.

The same precautions as to the accumulation of NH_4NO_3 in the anolyte were taken as in (iv.). The current was 1 ampère, and the anode area the same as for the preceding experiment. The results were exactly similar to those described in (iv.).

Analysis of the anode solid gave (a) 8.21, (b) 8.20 for the gold to oxygen ratio.

In this case also hydrated auric oxide is therefore formed. It is noteworthy that with acids of the concentrations used for (iv.) and (v.) no aurous compound is formed. Apparently the percentage of aurous compound in the solid formed at the anode decreases as the dilution of the nitric acid used for anolyte is increased, and finally a stage is reached beyond which practically pure hydrated auric oxide is produced.

If precautions are not taken to prevent accumulation of ammonium nitrate in the anolyte when dilute acids are used, a compound is formed at the anode which is violently explosive when heated. This compound is readily produced with an acid of concentration 1 cc. $\text{HNO}_3 \Delta 1.42$ to 20 cc. water; it is found intermixed with the hydrated auric oxide at the anode. At the stage at which this compound is formed a small quantity of black powder collects at the edges of the platinum cathode. This powder is gold. Hence under these conditions some gold cations are formed. Whether these are due to the decomposition of some complex ion has not yet been investigated, but it seems probable that a complex cation derived from gold and ammonium is formed.

Sulphuric Acid Electrolyte.

(i.). The concentration of acid used was that corresponding to 100 cc. H_2SO_4 of density 1.84, diluted with 100 cc. water. The temperature 18°C . to 20°C .

The platinum cathode was surrounded by a porous pot. The same acid was used for catholyte as for anolyte. The current was 2.5 ampères and the anode area $2 \times 11.74 \text{ cm}^2$. During the electrolysis the anode decreased in weight; no deposit was formed on the anode. The anolyte became of a deep olive-green colour, and gave an immediate precipitate of gold on the addition of SO_2 . A fine yellow powder was distributed throughout the anolyte; this was found to be pure gold. At this stage there was no trace of gold on the cathode.

Some of the green liquid was electrolysed, using a platinum anode and a platinum cathode surrounded by a porous pot containing dilute sulphuric acid. The gold was completely removed from the compounds in the anolyte and deposited on the anode; there was no trace of gold on the cathode.

It appears, therefore, that the gold from the gold anode goes into solution as complex ions.

The electrolysis with the gold anode was continued; the anolyte became of a bright yellow colour, and finally of a deep yellow-brown. There was increasing formation of the finely divided yellow gold throughout the anolyte.

At this stage there was a small deposit of gold on the anode. When this yellow-brown anolyte was electrolysed with platinum electrodes, as was done for the green anolyte, there was no decomposition of the gold compounds present.

The anode potential of the gold anode was taken during the electrolysis, using as normal electrode $\text{Hg} | \text{H}_2\text{SO}_4, 2\text{N}, \text{H}_2\text{SO}_4$, as described by Sand. For a steady current of 2.5 amperes this remained constant throughout the changes from the green to the dark yellow-brown stage and while the gold was deposited on the cathode.

It appears, therefore, that the gold goes into solution for the more part as complex anions, but that at the yellow-brown stage an appreciable quantity of cations are formed. None the less, the concentration of the cations in the neighbourhood of the anode must remain constant and very small. It is possible that the gold ions reaching the cathode may arise from the dissociation of the complex anions. A probable alternative is that some of the undissociated compound corresponding to the complex anions has diffused into the catholyte and has been reduced by the hydrogen at the cathode. The colour changes in the anolyte may be due to changes in the relative proportions of the complex anions and the undissociated compounds to which they correspond; the green colour is restored when the yellow-brown anolyte is diluted with sulphuric acid of the same concentration as originally taken for the anolyte.

Some of the yellow-brown anolyte was poured into a large volume of cold water at 15°C . The result of the hydrolysis was a red brown powder, which was washed for a considerable time until the washings gave no precipitate with BaCl_2 . It was then dried in a vacuum desiccator over concentrated H_2SO_4 for 80 hours. It was completely soluble in cold dilute HCl . This solution gave a small quantity of precipitate with BaCl_2 , but when the powder was heated with concentrated HCl no chlorine was evolved. There was, therefore, sulphate present, but no persulphate.

The powder heated alone gave gold, oxygen, and water and a small quantity of SO_3 . The gold to oxygen ratio was found. It was (a) 8.31 (b) 8.29, giving a mean 8.30—the ratio for hydrated $\text{Au}_2\text{O}_3 = 8.22$.

It is possible that the gold goes into solution in the trivalent and also in the monovalent state and that the product of hydrolysis contains a mixture of hydrated Au_2O_3 and of Au_2O . The ratio found corresponds to $\text{Au}_2\text{O}/\text{Au}_2\text{O}_3 = 0.01$. The presence of sulphate may be due to a basic auric sulphate, and the difficulty of washing free from sulphuric acid may be due to the slow hydrolysis of this basic sulphate when left under water.

The formation of finely divided gold distributed throughout the anolyte may be due to the transformation of an aurous compound in solution to an auric compound and gold; this may account likewise for the free gold which separates when the anolyte is kept in a closed flask.

(ii.). A less concentrated acid was used as electrolyte, formed from 1 cc. concentrated H_2SO_4 , density 1.84, diluted with 7 cc. water.

The same acid was used for anolyte as for catholyte. The current was 2 amperes and the anode area $2 \times 6.84 \text{ cm}^2$.

The anolyte became of a pale green colour, due to the formation of a gold compound; the anode was covered with a deposit of brown solid, which flaked off into the liquid. The cathode remained bright without a trace of gold. There was no free gold in the anolyte. After washing for three weeks the brown powder was dried over concentrated H_2SO_4 in a vacuum desiccator.

On heating it gave gold, oxygen, and water containing H_2SO_4 . It was completely soluble in cold dilute HCl , and this solution gave a small quantity of white precipitate with BaCl_2 ; no chlorine was evolved on heating the powder with concentrated HCl .

The mean value of the gold to oxygen ratio was 8.32.

The brown solid dissolved in cold concentrated H_2SO_4 diluted with an equal volume of water, giving a green solution like the green anolyte in (i.); this green solution, when electrolysed with platinum anode and platinum cathode surrounded by a porous pot containing dilute H_2SO_4 , was decomposed, giving a deposit of pure gold on the anode—there was no trace of gold on the cathode. The compound formed by this solution must therefore contain the gold as complex anions. The brown solid was left under a large quantity of KHCO_3 solution at room temperature for thirteen weeks. Part of the solid was dissolved, giving a yellow solution, from which yellow crystals were obtained by allowing the solution to evaporate in a vacuum desiccator over concentrated H_2SO_4 . The residue was a dark purple solid, which when washed reacted with dilute HCl to giving HAuCl_4 and gold.

It therefore appears that the brown powder is a mixture of hydrated auric oxide and Au_2O . The sulphate present is probably a basic auric sulphate which is slowly hydrolysed by water. The ratio found corresponds to $\text{Au}_2\text{O}/\text{Au}_2\text{O}_3 = 0.02$.

These results seem consistent with the hypothesis that a mixture of auric and aurous compounds is formed by the electrolysis with a gold anode, and that with an acid of this concentration the soluble complex gold compounds cannot reach so high a concentration as in (i.), owing to the greater percentage of water present in the anolyte.

Orthophosphoric Acid Electrolyte.

The concentration of the acid used was approximately 15 per cent H_3PO_4 by weight. The same concentration was used for the anolyte as for the catholyte initially, but during the electrolysis there was considerable transference of water from the anolyte to the porous pot. The level of the liquid in the pot had to be maintained constant by means of a capillary syphon, and to compensate the loss of water from the anolyte distilled water was arranged to flow into the anolyte so as to keep it at constant level.

The current used was 1 ampere, and the anode area was $2 \times 6.84 \text{ cm}^2$.

No gold was deposited on the cathode. The anolyte was filtered, and on being concentrated by heating gave a small quantity of purple gold.

A brown solid was formed on the anode and flaked off into the beaker containing the anolyte. The anolyte remained colourless.

It appears, therefore, that the gold anode does not give rise to cations, but that a very small quantity of gold goes into solution as complex anions.

The brown solid was washed for about three weeks until water left on it for two hours gave no reaction with ammonium molybdate; it was then dried over concentrated H_2SO_4 in a vacuum desiccator.

When heated the solid gave gold, oxygen, and water which was slightly acid to litmus. The gold to oxygen ratio was determined by heating the solid and collecting the oxygen. It was 8.58.

The brown solid was completely soluble in cold dilute HCl . About 4 grms. of the solid washed as described above were left in water and stirred, the water being frequently changed; this was continued for twenty-four weeks. The water was tested every week for H_3PO_4 ; for long a precipitate was obtained with ammonium molybdate, the quantity of which decreased with successive changes of the water. Finally no trace of H_3PO_4 could be detected in the water.

The solid was dried over concentrated H_2SO_4 in a vacuum desiccator and analysed. The gold to oxygen ratio was found to be (a) 8.62, (b) 8.60, giving a mean 8.61.

The water evolved on heating the solid was faintly acid to litmus.

It appears, therefore, that the quantity of the compound which gives H_3PO_4 with the water evolved on heating is

a very small fraction of the total weight of solid, and that this compound is very difficult to hydrolyse completely.

About 3 grms. of the solid was stirred continually with cold KOH solution. Nearly all the solid dissolved, but a small blackish residue insoluble in KOH solution was obtained. This with dilute HCl gave HAuCl_4 , and the gold was therefore aurous oxide.

Hence the solid product at the anode consists of a mixture of hydrated auric oxide and aurous oxide; the ratio 8.58 corresponds to $\text{Au}_2\text{O}/\text{Au}_2\text{O}_3 = 0.07$.

An acid of concentration approximately 20 per cent H_3PO_4 gave a solid of ratio 8.87, corresponding to $\text{Au}_2\text{O}/\text{Au}_2\text{O}_3 = 0.09$.

In all cases where a porous pot was used to enclose the cathode the outside of the pot was covered with a purple coloration where it was in contact with the anolyte. This purple coloration penetrated for a considerable distance into the wall of the pot when the pot had been used for a series of experiments. The purple coloration was due to gold. In order to see whether this could be caused by the action of the pot on the anolyte containing complex gold ions independently of the current passing, an unused pot was broken and fragments left in beakers containing portions of the various anolytes. In all cases there was a deposition of purple gold. The same took place when the fragments had been previously heated red-hot so as to destroy any organic matter.

In these experiments with the gold anode the composition of the gold products formed does not seem to depend on the anode current density employed, but it is influenced by the concentration of the acid used for the anolyte. It was impossible to maintain this concentration constant, as the acid anions continually moved from the catholyte into the anolyte when the current was passing. In order to minimise the changes in concentration the volume of the anolyte used was large, and except in the cases of the nitric acid and sulphuric acid solutions which did not give solid gold compounds, the anolyte acid was changed after a few hours. In the cases of the nitric acid and sulphuric acid solutions which did not give any solid compounds at the anode, it was necessary to use the same anolyte acid continuously in order to observe the progressive colour changes.

The idea of experimenting with a gold anode was suggested to me by Colonel C. T. Heycock, M.A., F.R.S., Goldsmiths Reader in Metallurgy; I am much indebted to him for his suggestion, and likewise for his kindness in giving me facilities for doing the work.

STUDIES IN THE STEREOCHEMISTRY OF QUINQUEVALENT NITROGEN.*

RESOLUTION OF THE ASYMMETRIC QUATERNARY AMMONIUM COMPOUNDS.

By SHIGERU KOMATSU.

(Continued from p. 219).

EXPERIMENTAL PART.

1. Dextro-camphorsulphonic Acid, $\text{C}_{10}\text{H}_{15}\text{O} \cdot \text{SO}_3\text{H}$.

The substance was prepared by Reychler's method (*Bull. Soc. Chim.*, 1898, [III.], xix., 120), and the process will be mentioned below.

152 parts Japan camphor purified by sublimation were treated with the mixture of 204 parts acetic anhydride from Merck and 98 parts pure concentrated sulphuric acid. After a while dextro-camphorsulphonic acid crystallised out in needles, which were separated from the mother-liquor by filtration, washed with ether, and then re-crystallised from acetic acid. The substance

dried at 100° for three hours, and observed to melt at 192 to 193° , was analysed, and gave the following results:—
0.1953 grm. substance gave 0.1916 grm. BaSO_4 .

Sulphur calculated for $\text{C}_{10}\text{H}_{15}\text{O}_4\text{S}$ 13.79
Sulphur found 13.46

The optical rotation of the free acid in an aqueous solution was determined:—

A solution of 0.8751 grm. acid made up to 25 cc. with water at 25° , gave $\alpha_D^{25} = +1.62^\circ$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +23.14^\circ$.

2. Lævo-camphorsulphonic Acid, $\text{C}_{10}\text{H}_{15}\text{O} \cdot \text{SO}_3\text{H}$.

l Camphor prepared according to Pope and Harvey (*Journ. Chem. Soc.*, 1901, lxxix., 76) from l borneol from Kahlbaum by oxidation with nitric acid (sp. gr. 1.42) was converted into lævo-camphorsulphonic acid by the usual way.

The acid purified by crystallisation from acetic acid was found to melt at 190° . Converting it into the ammonium salt, its analysis and optical determination were carried on, with the following results:—

0.4098 grm. substance gave 0.3896 grm. BaSO_4 .

Sulphur calculated for $\text{C}_{10}\text{H}_{15}\text{O}_4\text{SN}$ 13.61
Sulphur found 13.06

A solution of 0.3981 grm. of the ammonium salt made up to 25 cc. with water at 25° gave $\alpha_D^{25} = -0.68^\circ$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -21.35^\circ$. Pope and Harvey gave for its value $[\alpha]_D = -20.7^\circ$.

3. Dextro-bromocamphorsulphonic Acid and its Salts.

The following experiments were conducted according to the method suggested by Marsh and Cousins (*Journ. Chem. Soc.*, 1891, lix., 970). To prepare the acid, 100 grms. dextro-bromocamphor purified by re-crystallisation from methylated alcoholic solution and dissolved in 200 grms. pure dried chloroform were mixed with 75 grms. of fresh distilled chlorosulphonic acid, prepared after Muller (*Ber.*, 1878, vi., 227), and the whole contents of a vessel were heated over a water-bath for fifteen hours. The brown solution was then poured into cold water, and the chloroform separated from the brownish yellow aqueous part. The acidic aqueous solution was neutralised with calcium carbonate; removing calcium sulphate by filtration, a brownish yellow solution containing crude calcium bromocamphorsulphonate was obtained. The calcium salt was converted into the ammonium salt which crystallised out from hot water in white needle-shaped crystals.

The analysis of the pure ammonium salt gave the following value for sulphur:—

0.1996 grm. substance gave 0.1274 grm. BaSO_4 .

Sulphur calculated for $\text{C}_{10}\text{H}_{15}\text{O}_4\text{NSBr}$ 9.76
Sulphur found 9.74

A solution of 1.27 grms. of the ammonium salt made up to 25 cc. with water at 25° , gave $\alpha_D^{25} = +8.69^\circ$ in a 20 cm. tube, whence $[\alpha]_D^{25} = +85.54^\circ$ and $[\text{M}]_D^{25} = +280.59^\circ$, while Marsh and Cousins (*Journ. Chem. Soc.*, 1891, lix., 966) gave $[\alpha]_D^{25} = +87.52^\circ$, and Kipping and Pone (*Ibid.*, 1895, xvii., 354) $[\alpha]_D^{25} = +84.78^\circ$ for its specific rotation in the aqueous solution.

Starting from the ammonium salt the author has prepared the barium salt, free acid, and silver salt successively, and used the silver salt for the resolution of the asymmetric ammonium iodide.

4. Resolution of Methyl n-Propyl Phenyl Benzyl Ammonium Iodide into its Optically Active Components.

A. Lævo Methyl n-Propyl Phenyl Benzyl Ammonium Dextro-bromocamphorsulphonate, —

$(\text{CH}_3)(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5)(\text{C}_7\text{H}_7)\text{N} \cdot \text{O} \cdot \text{SO}_2 \cdot \text{C}_{10}\text{H}_{14}\text{BrO}$.
 $\text{CH}_3 \cdot \text{CO}_2 \cdot \text{C}_2\text{H}_5$.

One molecule of methyl n-propyl phenyl benzyl ammonium iodide, prepared from methyl n-propyl aniline and benzyl iodide, was mixed with one molecule of anhydrous

* *Memoirs of the College of Science, Kyoto Imperial University*, 1915, i, No. 5.

silver dextro-bromocamphorsulphonate, and boiled in a mixture of acetone and ethyl acetate for two hours over a water-bath. After the reaction had been completed, the silver iodide was separated, the solvent distilled off, and a brown syrupy residue allowed to stand, solidifying in a crystalline mass. The crystalline mass thus formed was dissolved in acetone, from which white crystals were obtained. The crystals purified by re-crystallisation from acetone, melted at 141° to 142° , and were analysed:—

0.235 grm. of the substance gave 0.1028 grm. BaSO_4 .

Sulphur calculated for $\text{C}_{27}\text{H}_{36}\text{O}_4\text{NSBr}$.. 5.81
Sulphur found 6.01

The rotatory power of the pure preparations *a* and *b* was determined in the aqueous solutions with the following results:—

(a). A solution of 0.866 grm. substance made up to 25 cc. with water at 25° , gave $\alpha_D^{25} = +3.50^{\circ}$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +51.68^{\circ}$ and $[M]_D^{25} = +284.2^{\circ}$.

(b). A solution of 0.7021 grm. substance made up to 25 cc. with water at 25° , gave $\alpha_D^{25} = +3.15^{\circ}$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +56.26^{\circ}$.

From the analytical results and polarimetric measurements above stated, it is quite evident that the substance would be the racemic one from which racemic methyl *n*-propyl phenyl benzyl ammonium iodide has been derived, as will be shown in the following polarimetric experiment:—

A solution of 0.1084 grm. of the iodide made up to 25 cc. with alcohol at 25° , gave $\alpha_D^{25} = +0.02^{\circ}$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +1.4^{\circ}$.

By the fractional crystallisation of the racemic bromocamphorsulphonate in ethyl acetate, laevo methyl *n*-propyl phenyl benzyl ammonium dextro-bromocamphorsulphonate separated out in white needle-shaped crystals, and the mother-liquor, on evaporation, yielded platy crystals; adding ether to the second filtrate, the third crop in the hygroscopic crystals, and finally a syrupy residue were obtained. To the latter, dissolved in water, was added an excess of a potassium iodide solution to precipitate the base as iodide.

The rotatory power of the crystallised fractions above mentioned was determined in their aqueous solutions, and the results will be shown as follows:—

I. The First Fraction, re-crystallised from ethyl acetate three times:—A solution of 1.1807 grm. substance made up to 25 cc. with water at 25° , gave $[\alpha]_D^{25} = -0.14^{\circ}$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -1.48^{\circ}$.

2. The Second Fraction.—A solution of 0.5738 grm. of the substance made up to 25 cc. with water at 25° , gave $\alpha_D^{25} = -0.04^{\circ}$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -0.09^{\circ}$.

3. The Third Fraction.—A solution of 0.7836 grm. of the substance made up to 25 cc. with water at 25° , gave $\alpha_D^{25} = +0.15^{\circ}$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +2.07^{\circ}$.

In order to fix the optical rotation constant, the first crop was re-crystallised several times from ethyl acetate, and the rotatory powers of the purified different preparations were determined in aqueous solutions and the results will be seen in the following statements:—

(a). A solution of 0.8157 grm. of the substance made up to 25 cc. with water at 25° , gave $\alpha_D^{25} = -0.16^{\circ}$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -2.45^{\circ}$.

(b). A solution of 0.6316 grm. of the substance made up to 25 cc. with water at 25° , gave $\alpha_D^{25} = -0.13^{\circ}$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -2.57^{\circ}$.

Pure laevo methyl *n*-propyl phenyl benzyl ammonium dextro-bromocamphorsulphonate has the mean specific rotatory power $[\alpha]_D^{25} = -2.51^{\circ}$ in an aqueous solution, but no definite melting-point; it was soluble in acetone, ethyl acetate, alcohol, and water, but not in ether.

Since the crystals when heated at 80° became opaque, the author was led to the suspicion that they might contain solvent in the molecule.

When 1.419 grm. of the pure crystals obtained from the ethyl acetate solution were heated in an air-bath at 80° for

five hours, it was observed that the loss of weight amounted to 0.1821 grm., which just corresponds to the calculated value of ethyl acetate of crystallisation (one molecule) for one molecule of the active substance.

Ethyl acetate calculated for
 $\text{C}_{20}\text{H}_{36}\text{O}_4\text{NSBr} \cdot \text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$ 13.79
Ethyl acetate found 12.83

The substance gave the following analytical result:—

0.27 grm. of the substance gave 0.0385 grm. BaSO_4 .

Sulphur calculated for $\text{C}_{31}\text{H}_{42}\text{O}_6\text{NSBr}$.. 5.02
Sulphur found 5.02

(To be continued).

RADIOMETRIC MEASUREMENTS OF THE IONISATION CONSTANTS OF INDICATORS.*

By E. J. SCHAEFFER, M. G. PAULUS, and HARRY C. JONES.

(Continued from p. 209).

Experimental Work on Methyl Orange.—Before discussing the tables showing the results of the calculations based on the above deductions, it will perhaps be of interest to consider a few of the more important results of the preliminary work on methyl orange. Two mother solutions of known concentrations were prepared, the one being methyl orange and the other sulphuric acid. All solutions were made up at 20° , and carefully purified substances dissolved in conductivity water were employed in all cases. A number of test solutions were prepared from the mother solutions, all of which contain equal amounts of methyl orange but different amounts of sulphuric acid. The volume of each solution was 100 cc. The solutions thus presented a series of colour shades, ranging from yellow to deep red. The percentage transmissions I/I_0 were taken with a 20 mm. depth of each solution for the same four or five wave lengths of light. The region of the spectrum to be studied is given by the ascending arm of the transmission curve for methyl orange. This region for the above-named indicator is between $\lambda = 0.56 \mu$ and $\lambda = 0.59 \mu$. The radio-micrometer deflections in this region are necessarily small, and certain variations which appear in the data can be explained in a large measure as due to the vibrations of the building, which often prevented accurate readings.

Special attention is called to a solution of methyl orange containing an excess of alkali and another solution containing an excess of acid. Equation 19 shows that the calculation of c depends not only on the percentage transmission of the solution in question, but also on the percentage transmission for a solution in which all of the methyl orange exists as the azo-base, and one in which all of the indicator has been converted into the quinoid salt. It is thus necessary to know if any alkali must be added to convert all of the methyl orange into the azo-base and to prevent hydrolysis, and also how much acid is required to form the quinoid salt and to completely suppress hydrolysis. Furthermore, the stability of these solutions must be considered.

Table II. shows that in a pure aqueous solution of methyl orange there is no appreciable hydrolysis, and that practically all of the indicator exists as the azo-base. It is therefore not necessary to add alkali in determining the value of $(I/I_0)'$ in Equation 19. The volume of all solutions used in Table II. was 100 cc., and each solution contained the same amount of methyl orange.

I. Methyl orange in pure water.

II. Methyl orange + 1 cc. N sodium hydroxide.

III. Methyl orange + 2.5 cc. N sodium hydroxide.

* From the *Journal of the American Chemical Society*, xxxvii., No. 4.

TABLE II.

I, I₀ for depth of solution = 20 mm.

$\lambda = \text{A. U.}$	I.	II.	III.
5648	70.3	71.2	70.5
5698	79.3	78.8	79.0
5748	84.6	86.0	84.8
5797	90.0	90.0	88.5
5847	91.4	92.2	90.0

Table III. gives results for three solutions of methyl orange, each containing an excess of acid and the same amount of indicator diluted to 100 cc.

I. Methyl orange + 0.2 cc. concentrated sulphuric acid.

II. Methyl orange + 0.5 cc. concentrated sulphuric acid.

III. Methyl orange + 1.0 cc. concentrated sulphuric acid.

TABLE III.

I, I₀ for depth of solution = 20 mm.

$\lambda = \text{A. U.}$	I.	II.	III.
5698	15.2	15.2	16.6
5723	20.2	20.1	20.1
5748	30.7	31.2	31.9
5773	39.5	39.2	38.8
5797	48.7	49.2	48.1
5823	55.0	53.8	55.3
5847	61.4	62.6	63.2

It is obvious from Table III. that 0.2 cc. of the acid is sufficient to convert all of the azo-base into the quinoid salt and to suppress hydrolysis completely.

Stable solutions of methyl orange are given only when the concentration is less than 2×10^{-4} gram. molecules per litre. Considerable difficulty was encountered during the preliminary work owing to the fact that the indicator solutions were more concentrated than the above named limit. Such solutions of methyl orange, especially those containing a large excess of acid, and also those with enough acid to give an intense red colour, gradually become more transparent on standing. The action of light very greatly accelerates this bleaching process. The solutions most susceptible to the action of light and of time are those containing the greatest amounts of acid. It was found that these solutions could be kept in the dark for four or five hours unchanged, and that as soon as they were exposed to the light bleaching again took place. Experiments were made which showed that light of the shorter wave lengths was more active in increasing the transparency of the solutions than light of longer wave lengths. The addition of 10 per cent of ethyl alcohol rendered these solutions fairly stable against the action of light and time. After standing for a day or two solutions containing an excess of acid often showed the presence of fine crystals. Large amounts of these crystals could be obtained by strongly acidifying a saturated solution of methyl orange. It is thought that the formation of these crystals, very probably helianthine itself, causes the instability of the solutions in question. The obvious procedure to follow was to use more dilute solutions, which were found to be quite stable, and even the solution containing the excess of acid would remain practically unchanged when exposed to the action of light for a short time. However, when the concentration of methyl orange approximated 2×10^{-4} gram.-molecules per litre, as is the case for the solutions given in Table IV., the solution containing an excess of acid was prepared last and its percentage transmission measured immediately. The remaining solutions were kept in the dark until used. It is certain that when such precautions are taken no appreciable change in transparency could occur before the radiometric measurements were completed. Table III., the concentration of the methyl orange being 1.98×10^{-4} gram.-molecules per litre, shows that even the solutions containing an excess of acid can be safely used in this way.

The following shows how accurately small concentrations of hydrogen and hydroxyl ions can be estimated by radiometric measurements. If the percentage transmission for the various solutions be plotted as curves, the abscissa being wave lengths and the ordinates percentage transmissions, it will be noted that with increasing amounts of acid the transmission curve for pure methyl orange is widely displaced towards the red end of the spectrum. The solution curve corresponding to the excess of acid is displaced about 400 Angstrom units from the curve corresponding to a pure aqueous solution of methyl orange. From the displacements produced by solutions containing known amounts of acid, and the displacement given by a solution containing an unknown amount, the concentration of the unknown amount of acid can be quite accurately and quickly determined. In one case a solution was prepared containing an amount of sulphuric acid unknown to us. The concentration of the acid was determined by the above method, and the value found was 0.00000216 gram. per cc. The amount actually present was 0.00000210 gram. per cc. Several similar attempts were made, and they were quite as successful.

(To be continued).

NOTICES OF BOOKS.

Practical Organic and Bio-chemistry. By R. H. A. PLIMMER. London, New York, Bombay, Calcutta, and Madras: Longmans, Green, and Co. 1915.

THIS book is a fresh edition under a new name of the author's "Practical Physiological Chemistry," which was originally compiled as a handbook for practical work for the use of the students of University College, London. Its scope has been greatly extended and much new matter has been added. Thus, methods employed in more advanced work are now included, and sections on organic chemistry and on organic substances in plants have been inserted. Indications are given of the experiments which are suitable for a preliminary course, and the more elementary portions of the book are distinguished from the more advanced by differences in type. The author shows much skill in his descriptions of the more elaborate practical methods, which are so clear that the student will probably find all his difficulties forestalled, and the book is unsurpassed in the English language as a text-book of practical bio-chemistry.

Industrial Nitrogen Compounds and Explosives. By GEOFFREY MARTIN, Ph.D., D.Sc., B.Sc., and WILLIAM BARBOUR, M.A., B.Sc., F.I.C., F.C.S. London: Crosby Lockwood and Son. 1915.

THIS manual, which belongs to the series of manuals of technology edited by Dr. Geoffrey Martin, deals with a group of substances which is of enormous and rapidly growing importance, and describes modern processes of manufacture and uses with considerable completeness. The necessity for preparing nitric acid and nitrates in Great Britain is very urgent, and those who are interested in the subject will find that in this book special attention is paid to recent methods, and patent literature has been carefully summarised. The ammonia industry and synthetic methods of preparation are treated very fully, and a comparatively large portion of the book is devoted to the consideration of the manufacture of explosives. This section has been written by Mr. W. Barbour, who has had extensive experience in the explosives industry. The book is fully illustrated with clear diagrams, and is well printed and free from errors, although ammonium carbamate is described as ammonium carbonate in one place.

Organisation Scientifique. FREDERIC W. TAYLOR, 1856—1915. ("Scientific Organisation.") By HENRY LE CHATELIER. Paris: Dunod et Pinat. 1915.

IN this volume, which consists of lengthy extracts from the *Revue de Métallurgie*, an account is given of the work of the late F. W. Taylor, and M. Le Chatelier subjects his system of scientific management to a critical examination and discussion. The essential principles of the scheme are very clearly explained, and the remarkably original nature of Taylor's work and ideas is fully realised. Many important memoirs on the system have been brought together in the volume, and a short *résumé* of their contents is usually given. At a moment when we as a nation have to think very seriously about "setting our house in order" the theories of the great American engineer have a vital interest, and this highly appreciative survey may be recommended as giving a clear view of them.

Quantitative Chemical Analysis. By NICHOLAS KNIGHT, A.M., Ph.D. Revised Edition. New York and Chicago: The A. S. Barnes Company. 1915.

IN this introduction to quantitative analysis a short course of gravimetric and volumetric work is given, graduated in difficulty, but so arranged that practically any of the sections may be omitted as it suits the student. The directions for performing the experiments are very concisely and clearly worded, and the importance of cleanliness and careful attention to detail is very rightly emphasised; high ideals of accuracy and thoughtfulness are kept before the student, whose work should benefit greatly by the use of the book. Various minerals have been chosen to exemplify the processes of gravimetric analysis, and most of the usual methods of separating a mixture and determining its constituents are described. The examples have been carefully selected to give the student good practice in manipulation and the performance of estimations, and to make him acquainted with a wide range of methods. Volumetric work is similarly treated very satisfactorily and some typical processes are described, beginning with titrations with permanganate. A short section deals with the analysis of ordinary drinking water for the usual impurities, in which full details are given for the preparation of all the solutions and the carrying out of the tests.

Northampton Polytechnic Institute. Announcements Educational and Social for the Session 1915-1916.

THE Governing Body of the Northampton Polytechnic Institute has decided that the regular classes which have been announced for previous sessions shall be continued, although some modifications have been thought necessary. Thus the second and third year courses in the Engineering Day College are to begin in January and to be continued till July, and thus students will be able to work until Christmas in the munitions workshop, which has been fully occupied in making gauges and parts of armaments during the whole of the summer vacation. Some special series of advanced lectures in engineering have had to be dropped, but a new evening glass workers course has been started. In the Mechanical Engineering Department the testing equipment has been increased by the addition of a Heenan and Froude dynamometer and the prime mover equipment by a semi-Diesel engine. In the Electrical Engineering Department various transformers and motors of special types have been added, and a Tirrell regulator and a mercury arc rectifier have been installed. In other departments also the equipment has been extended. In all departments, Engineering, Artistic Crafts, Technical Optics, Technical Chemistry, Horology, and Women's Trades, the programmes of the various classes have all been brought up to date.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxi. No. 12, September 20, 1915.

Action of Ultra-violet Rays upon Solutions of Mercuric Chloride and of some Mercury Salts.—Jean Pougnet.—When a 5 per cent solution of mercuric chloride in water is exposed to ultra-violet light it becomes turbid almost instantaneously, and the heavy white precipitate deposited consists of calomel. If estimations of the amount of mercuric chloride remaining are made every ten minutes at first and then every twenty minutes, it is found that the action begins rapidly, then slackens, and passes through a minimum. The action is reversible, the calomel formed giving HgCl_2 and Hg by photolysis. Most other salts of mercury are affected by ultra-violet light; the perfectly dry salts resist it best.

MISCELLANEOUS.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 1st inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Resolutions of Thanks passed to Mr. Richard Pearce for his donation of £100 to the Fund for the Promotion of Experimental Research at Low Temperatures, and to Mrs. Hugo Müller for her present of a Microscope. Mr. Wilfrid Ward, F.S.A., was elected a Member. Resolutions of Condolence were passed with the relatives of the late Mr. William Hugh Spottiswoode and Sir Andrew Noble, Bart.

Royal Institution.—The Ninetieth Illustrated Christmas Course of Juvenile Lectures, founded at the Royal Institution in 1826 by Michael Faraday, will be delivered this year by Prof. H. H. Turner, D.Sc., D.C.L., F.R.S., his title being "Wireless Messages from the Stars." The subjects are as follows:—How the Messages are Carried, Tuesday, December 28; How the Messages are Received, Thursday, December 30; First Message, "We are very far away," Saturday, January 1; Second Message, "Some of us are Giants and some are Dwarfs," Tuesday, January 4; Third Message, "But we all behave much as you do," Thursday, January 6; Fourth Message, "And in fact we are your Blood Relations," Saturday, January 8. The lecture hour is three o'clock.

MEETINGS FOR THE WEEK.

MONDAY, 8th.—Biochemical Society, 530. (In the Physiological Department, King's College, London). "Distribution of Iodine in Plant and Animal Tissues," by A. T. Cameron. "Volumetric Estimation of Total Sulphur and Sulphates in small Quantities of Urine," by J. C. Drummond. "Action of Diabetic Blood on Sugar" and "Observations on the Quantitative Determination of Carbohydrates by means of the Ordinary Alkaline Copper Solutions," by H. Maclean. "Separation of Creatinine and Methylguanidine by the Silver Method," by A. J. Ewins.

THURSDAY, 11th.—Royal Society. "Effects of Function Activity in Striated Muscle and the Submaxillary Gland," by J. Barcroft and T. Kato. "Studies on a priori Pathomeiry," by Sir K. Ross. "The Spread of the Excitatory Process in the Vertebrate Heart—Part I, The Tard's Ventricle; Part II, The Tortoise Ventricle; Part III, The Dog's Ventricle; Part IV, The Bird's Heart; Part V, The Human Ventricle," by T. Lewis. "Analyses of Agricultural Yield—Part II, The Sowing-date Experiment with Egyptian Cotton, 1913," by W. L. Balls and F. S. Holton. "On Williamsoniella, a New Type of Bennettitalean Flower," by H. H. Thomas.

THE CHEMICAL NEWS.

Vol. CXII., No. 2920.

THE YIELD OF PAPER ON GREEN STEM OF BANANA.

By CLAYTON BEADLE and HENRY P. STEVENS.

As a general rule, materials such as crop plants, when tested to determine their value for paper-making, are sent over in the form of dried stems, generally gathered on the field in the green state and dried before being sent off, or in some few cases in the form of "dressed" fibre prepared by combing the green stems or passing them through crushing rollers, and drying. All analytical figures in such cases have to be calculated upon the weight of the plant as received. All such figures, although valuable in themselves, lose most of their practical utility when applied to green crop plants such as the banana; in fact, green crop plants in general. Moreover, the mere fact that the banana stem is capable of being converted into paper and is at the same time a waste and hitherto unutilised product is of little practical importance unless it is taken in conjunction with the cost of gathering and transport of the green stems from the field to a centre or locality where it can be dealt with. On this point no opinion can be formed until some knowledge is obtained of the yield of paper or pulp on the green weight of the stem.

This particular point of view appears never to have been sufficiently considered when discussing the possibilities of certain classes of fibres, such as green crop plants, for the manufacture of paper. The class of fibre to which we refer is typified, for instance, by the banana which has been so frequently experimented upon for the manufacture of paper on account of the enormous quantities of banana plants which go to waste. If a plant like the banana is to be used in the manufacture of paper, it must be either taken in the dried state and transported to some locality where the whole of the dried plant is converted into paper, or it must be transported in the green state to some centre where the same operation can be conducted. Or, if it is to be shipped, in addition to reaping and gathering it would have to be passed through crushing rollers, dried, and baled. It is difficult to conceive how these operations could be carried out on the field, and, by whatever method the fibre is obtained, it is of great importance to form an estimate of the amount of green material which would have to be handled to produce a ton of paper. With a view to arriving at some conclusion in regard to this point, we have constructed the accompanying table, which gives in Column 1 the percentage of fibre obtained on the green weight, Column 2 the number of tons of green weight that would have to be handled to yield a ton of dressed fibre, Column 3 the approximate number of tons of green weight which would have to be handled and transported per ton of paper produced. These results have been gathered together from different sources. The mean figure for the green weight to be handled is no less than 132 tons per ton of paper produced. This assumes a production of paper equal to half the dry weight of the raw fibre. This is a figure which for this class of paper we find to be a very reasonable assumption. It is quite evident that the mere reaping, gathering, and transporting, even for a short distance, of such large weight of green stem would render the cost of getting together large supplies of these materials absolutely prohibitive.

If the material is merely dried upon the field and then transported in the dry state, without dressing or washing, the yield is very disappointing. In the case of a fibre of this description which, when passed through crushing rollers and dried, yielded between 50 and 60 per cent of paper on

the dry weight of the fibre. The same material when dried on the field like making hay, and then treated chemically by conversion into paper, only yielded 32 per cent. The crushed and dried material consumed 6 per cent of alkali on the weight of the paper produced, whereas the plant dried without washing, by reason of the fact that it contained much material which had to be got rid of and which would otherwise have been removed by the crushing mills, consumed 18 per cent of soda, also calculated on the weight of paper produced. It is quite evident, therefore, that fibre of this class would have to undergo some mechanical process of treatment on the field or at some convenient collecting centre, very near to the gathering ground, in order that the chemical treatment could be effected in an economical manner.

TABLE.—Summarising Field Trials on Yield of Fibre on Green Stem and Approximate Amount of Green Stem required to produce One Ton of Paper.

	New Bulletin .		Tons of	Dressed	Tons of
	I. Vegetable		green	fibre on	green
	Fibres.		weight	green	weight
			per ton	weight of	per ton
			of paper.	plant.	of fibre.
	Page.	Line.	Per cent.		
<i>Musa textilis</i>	97	6	1.49	67	134
	97	31	1.66	60	120
	98	15	1.44	70	140
Banana	98	22	1.02	98	196
	98	28	1.44	70	140
	98	39	1.81	53	110
Plantain	98	41	2.25	44	88
<i>Musa</i>	98	49	1.87	53	106
<i>Musa ensata</i>	99	10	1.16	86	172
<i>Musa sapientum</i> (var.					
<i>paradisica</i>)					
Plantain	103	46	1.14	70	140
	103	48	1.81	53	110
Average			66.2	132.4	

ON THE ELECTROLYSIS OF CONCENTRATED HYDROCHLORIC ACIDS USING A COPPER ANODE.*

By F. H. JEFFERY, M.A.

THE apparatus was similar to that employed for the experiments with the gold anode, save that the beaker, porous pot, and electrodes were enclosed in a bell-jar over water, so that the electrolysis might be performed in an atmosphere of nitrogen. The anolyte was stirred as previously.

The current used was 0.5 ampère. No copper was deposited on the cathode, nor was there any trace of copper compound in the catholyte after six hours' steady current.

The anolyte became slightly yellow, and there was a considerable quantity of a fine blackish powder on the bottom of the beaker and on the anode. There was also a sediment of white powder. The black powder was found to be metallic copper, due to the disintegration of the anode.

The white powder was cuprous chloride. No chlorine was evolved during the electrolysis.

The anolyte gave a white precipitate of cuprous chloride on addition of water; with sodium hydroxide solution it gave a yellow precipitate of cuprous hydroxide; with ammonium hydroxide it gave a gradually deepening blue coloration on shaking in the air.

It appears, therefore, that the copper goes into solution as complex anions, and as excess of hydrochloric acid is present these are the ions corresponding to H_2CuCl_3 .

* Reprint of selected papers from the *New Bulletin*, Additional Series II.

† A Paper read before the Faraday Society, October 19, 1915.

As the CuCl was formed towards the end of the electrolysis it may be that this reaction is represented by $\text{CuCl}_3 \rightleftharpoons \text{CuCl} + 2\text{Cl}^-$.

An alternative explanation would be that CuCl is ormed directly from the chloridion and the copper anode, and that this dissolves without dissociation in the hydrochloric acid present until a saturated solution is formed, when there is precipitation of CuCl on the bottom of the beaker as the electrolysis proceeds.

In order to test this latter hypothesis the following experiment was made. Starting with pure concentrated hydrochloric acid and a clean copper anode the electrolysis was performed for six hours with a steady current of 0.5 ampère. Then the current was stopped, but all other conditions, including the stirring, were maintained the same as when the current was passing. After three hours the catholyte was examined and it was found that some of the copper compound in the anolyte had diffused into the catholyte.

This could not have been prevented for six hours by the passage of the current unless the copper had been present as complex anion.

If the electrolysis was continued after some of the copper compound had diffused into the catholyte, copper was at once deposited on the cathode. This was due to the complex copper compound being reduced by the hydrogen at the cathode.

INTRODUCTION TO THE THEORY OF RELATIVITY.

By F. H. LORING.

(Continued from p. 227).

THE Michelson-Morley famous experiment, devised to detect any relative motion between the earth and the supposed æther, consisted briefly in passing a beam of light into a system of ordinary mirrors and a partly reflecting, partly transmitting plate, the light being directed in such a way that, in one orientation of the apparatus, the supposed æther (if not moving with the earth) would allow the aberration effect to take place, and give rise to interference phenomenon with another beam, which has travelled in the same system in a direction uninfluenced

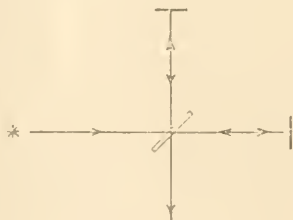


FIG. 3.

by the earth-movement. Fig. 3 shows the optical scheme. The entire apparatus was continuously rotated in one experiment to interchange the functions of the parts, and thus cancel out inevitable errors by giving a measurable or not difference in the fringes, should the supposed æther not move with the earth. The experimenters obtained negative results, however, pointing to the supposed æther moving *with* the earth. The shift for a 90° rotation on the basis of a stationary æther should have been quite appreciable, namely, four-tenths of a fringe width. This experiment is therefore in conflict with the aberration one observed with the light from the star, which seemed to indicate that the æther was stationary.

These various experiments can be apparently reconciled by not accepting the doctrine of an æther, or at least by leaving it out of account, and introducing the principle of relativity, but before coming to this theory it will be desirable to reconsider the last experiment cited.

Prof. Wood, in his book "Physical Optics," 1914, p. 675 (Macmillan), remarks:—"It is obvious that the failure of the earth's motion to influence in any way phenomena occurring in optical systems located wholly upon the earth are at once explained if we assume that the velocity of light is influenced by the motion of the source, i.e., if the velocities are additive, as would be the case in the corpuscular theory, for, in this case, the moving observer would remain at the centre of the wave. This [corpuscular] hypothesis has never been seriously considered, for it is incompatible with the wave-theory." The idea of added velocities is clear if it be assumed that the light pulse partakes of the movement of the light source. It is interesting to note that if the æther does not exist, a corpuscular-like theory of light is apparently necessary.

Returning to the ball analogy, and imagining things arranged to resemble in part the Michelson-Morley apparatus, the thrower of the ball may be considered as standing on a stationary platform car at one side. At the other side of the car a target is provided. Suppose that when the ball is thrown it will strike the target in a central spot A. Now suppose the car to be under uniform motion along a straight track. If the ball be again thrown with precision as before it will strike the spot A again. No aberrational effect has taken place. This is an imperfect representation of the light experiment in its entirety, but it will perhaps help to fix the idea of a moving source and light-pulse, considered as a sort of quantum, moving in (or with) what might be termed a self-contained system, or remaining in the centre of the wave. Prof. Wood goes on to say:—"In the last chapter we shall take up the whole matter from quite a new point of view, the theory of relativity, and it will be shown that from a certain point of view a moving source of light can be considered as remaining at the centre of the waves which it originates, which is all that we require."

The difficulty encountered in the case of the Michelson-Morley experiment in reconciling it with the star-aberration experiment has been tentatively removed by an ingenious suggestion that the apparatus contracts by a very minute amount along the direction of movement just sufficient to compensate the effect looked for due to the relative motion of the apparatus with respect to the supposed æther. This is known as the Lorenz-FitzGerald contraction hypothesis. This brings us now to the modern theory of relativity, and here too a most extraordinary conception is introduced that bids fair to have far-reaching consequences. Indeed, this theory is in some ways an extension of the great mathematical work of H. A. Lorentz, and H. Minkowski has adopted bodily Maxwell's classical equations in developing its exposition along rigorous mathematical lines involving the Lorentz transformation as developed in the electron theory.

It may be stated at the outset that this new theory almost of necessity abolishes the æther. Attempts to retain or consider somehow the æther (or æthers) have nevertheless been made (see, for example, Cunningham, "The Principle of Relativity," 1914, Cambridge University Press), but it does not appear that the idea of relativity coupled with that of an æther is consistent or necessary. It may turn out that the conception of the æther will have to be modified in its interpretation so as to stand for some extended state of matter and thus reconcile conflicting schools of thought. This idea does not really mean anything, because it is not worked out. It is not intended here to discuss issues of this kind. On the contrary, it is perhaps best to keep to the "orthodox" school of relativity, if this expression may be allowed. Quoting from a review of Dr. Silberstein's work "Theory of Relativity," 1914, in *Science Progress*, January, 1915:—

"One of the first results of the theory is the reduction of the æther to nothingness. For, as no system has any preference over any other with respect to the propagation of light, we are left with a choice between no æther at all, or, since every body may be considered as having an equal right to its own æther, a triple infinity of æthers—one supposition being as comforting as the other."

This theory involves taking a different view of the tacitly-accepted idea of the absoluteness or universality of *time, length, and space*: to keep to certain fundamentals. These conceptions are regarded from a certain point of view as collectively *relative*, so that, if a boy with a watch were to be transported to a different moving world of say another planetary system in space, he would find his conceptions of these fundamentals altered, provided he could retain some fixed background of reference for comparison. For example, his watch would be "running" at a different relative rate, and he himself, as a growing organism, would grow at a different relative rate. All these changes would be in proportion, so that he would not realise the "change," unless he could retain some one "thing" for reference. The æther cannot be a framework of reference, to use current phraseology, since that would be tantamount to giving it *preference*, as if it belonged to our particular world-system.

Thus it will be seen that nothing would be retained of our system that would afford an absolute framework of reference, and, if an æther were considered, it would have no preference, so to speak, for one world-system over another.

We are at a loss to see where we are with such an appalling conception, but when we realise that light phenomenon is essentially one that extends into the furthest reaches of space, we begin to get a glimpse of how these ideas can be put on a proper basis, and in harmony with the older ideas of the relative importance of things. Light, we may say, stands first on our list. Evidently, Einstein determined to make the universal propagation of light through empty space at a constant velocity the real philosophically fixed thing (or unique basis of, or tool for, measurement), then to define *time, length, and space* in terms of its equality as it were. The most brilliant conception in this theory is the *time-basis* as established by light signals (see examples to follow) from one body in space to another: the velocity of light being constant. This accomplishment results in time being dependent upon translational movement of the bodies, in, of course, a comparative sense, taking into account the light propagation itself as becoming a sort of "fixed" thing, since there is no absolute time-reference. Einstein makes *time* relative to, or dependent upon, the translational movement of bodies in space by defining it in terms of light-signals. That is to say, the flashing of a light-signal out into space from a system S to a system S', and back again from S' to S, is made the basis for synchronising or setting imaginary watches or clocks located on the bodies of these systems. Now if these respective bodies be moving towards each other ($\cdot \rightarrow \leftarrow \cdot$), or away from each other ($\leftarrow \cdot \rightarrow \cdot$) we should expect to make allowance for the changing light-distance, since one body gains or loses on the other—the distance traversed in carrying into effect the reciprocation in light-signals not being equal both ways, owing to the lapses of time in receiving and sending back signals while the positions of the bodies in space are changing—the general background of time then being the same everywhere. This is not what is done; the watches are "synchronised" by the light, according to the movements in such a way as to bring about or establish a different *relative* unit of time on the systems when they are in relative movement ($\cdot \rightarrow \leftarrow \cdot$ or $\leftarrow \cdot \rightarrow \cdot$).* When, however,

they are not moving relatively ($\cdot \cdot \cdot$), the unit of time, say the second, is the same by light signalling at each station; but the standard time from one point of view becomes altered when bodies are moving together (not towards each other) in space so as to change their positions with respect to the light disturbance, the movement being in a direction coincident with the line joining the bodies (see below). This means that to a stationary observer (one on a *third* system) the clocks or watches would not be together in time after being synchronised and set by the mutual observations (signals) between the first and second systems or bodies.

An altered unit of time involves alterations in other "fundamentals," and it was evidently owing partly to circumstance that *time* was made the variable as a first consideration. The principle is of wide significance. One of its chief postulates (the second one) involves consistently the principle of constant light-velocity regardless of the movement of the light source one way or another. Movement *this way or that way* becomes in a sense meaningless, since there is no particular choice of reference in the absolute sense, but there is *relative* movement. (The examples referred to above will be given in the next issue).

(To be continued).

THE TESTING OF ORES FOR THE CYANIDE PROCESS.

By WELTON J. CROOK.

Acidity.

SOLUTIONS of the alkaline cyanides are very easily decomposed by a multitude of substances and under many conditions. The hydrocyanic acid resulting from these decompositions is but sparingly soluble in water, and if the solution contains dissolved salts its solubility tends to be decreased. Hydrocyanic acid contains the active and useful elements which enter into the reactions which make the cyanide process possible, and these are lost by the volatilisation of the acid.

Among the substances which tend to decompose solutions of the alkaline cyanides are the mineral acids and their salts, the common ones being H_2SO_4 , H_2CO_3 , HCl , HNO_3 , FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, CaSO_4 , &c. Wood, jute, and cocoa fibre when new also have the same effect; lastly, the sulphides of iron and copper, especially if partly decomposed by weathering, are very active as decomposing agents. These groups of substances are called "cyanicides," and may be defined as "substances which decompose active cyanides, forming compounds which are not solvents of gold and silver." Many of these substances may be neutralised by the presence of soluble alkalis, and the term "acidity" as used in ore testing includes acids and salts which may be so neutralised.

Acidity may be readily divided into two classes:—(a) soluble acidity and (b) latent acidity. Soluble acidity is the acidity caused by soluble acids and salts soluble in water, while latent acidity is that caused by salts and substances not soluble in water, but which nevertheless are able to decompose alkalis. Latent acidity is largely due to the presence in the ore of certain basic salts and to the presence of undecomposed sulphides.

"Total" acidity includes the sum of both soluble and latent acidity.

In the treatment of ores having a very high soluble acidity preliminary water washes may be employed with advantage, and this is especially the case in treating weathered tailings containing iron and copper sulphides. It is then possible to remove if necessary a large part of the soluble acidity, so that the use of the added alkali is principally to overcome latent acidity. The substance which causes latent acidity decomposes cyanide but

* The movement must be *relative* to the bodies, since by this theory there is no stationary æther as a frame of reference, therefore one body may be considered stationary and all the movement confined to the other, although there is no way of distinguishing the particular one to be regarded as at rest.

slowly, and will react with any free alkali which may be present in preference to the alkali cyanide. It may therefore be said that alkali protects cyanide; hence the term "protective" alkalinity.

In the early day of the history of the cyanide practice much difference of opinion existed as to the best alkali to use as a neutralising agent for acidity. Caustic soda and lime were the most generally considered. Lime has several advantages in practice, among which are its cheapness, slow solubility, and the fact that 1 lb. of lime is as effective as 1.4 lbs. of caustic soda; also to the fact that it has great power of coagulating and settling slimes and turbid water.

However, in making laboratory tests for acidity lime is not as suitable a reagent as sodium or potassium hydroxide on account of its slow and slight solubility in water. In the tests outlined sodium or potassium hydroxide is accordingly used, and from the results obtained the equivalent amounts of lime are calculated. It will be shown further on in this article how this calculation may be made.

In making the acidity tests it is necessary to have two standard solutions, one an acid and one an alkali. It is most convenient to have them of equal strength, that is to say, 1 cc. of acid exactly equalling 1 cc. of alkali when titrated against each other, using phenolphthalein as an indicator.

The most convenient standard acid solution to use for this purpose is that of oxalic acid, as this may be standardised by weighing out the solid acid, and because it is also used in determining available calcium oxide in lime, as will be shown in the next instalment of this article. In this way it is readily possible to make a comparison between the standard solution of caustic alkali and the lime which will be used in subsequent tests on the ore.

It may be objected that a standard oxalic acid solution prepared by weighing the solid acid is not accurate owing to the uncertain hydration of the crystals, but it has been found that if the acid used is fresh and has been preserved in a carefully stoppered bottle the results obtained will be easily accurate enough for this use.

The standard acid solution is prepared by weighing out 14.6068 grms. of oxalic acid and dissolving in 1 litre of distilled water. Thereason for using acid of this strength is as follows:—The number of grms. of ore used in the acidity tests is calculated from the strength of the acid, but in order to simplify the explanation it is assumed that the weight of ore is known and the strength of acid unknown.

If lime is added at the rate of 1 lb. per ton of ore, then 1.2000 or 0.0005 times the weight of ore in lime is added for each pound per ton required. In making the tests 26 grms. of ore are agitated with 100 cc. of water and then filtered; the acidity in 50 cc. of the filtrate is then neutralised with the standardised alkali solution. The 50 cc. titrated contains the acidity from 13 grms. of ore. $13 \times 0.0005 = 0.0065$ gm. of lime to be added to 13 grms. of ore for each pound of lime required.

The combination of lime with oxalic acid is represented by the equation $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} + \text{CaO} = \text{CaC}_2\text{O}_4 + 3\text{H}_2\text{O}$. From which it is seen that 126 parts by weight of oxalic acid reacts with 56 parts by weight of CaO; therefore the weight of oxalic acid which combines with 0.0065 gm. of CaO is found by the proportion—

$$0.0065 : 56 :: x : 126 \quad x = 0.0146068.$$

Therefore 0.0146068 gm. of acid are to be contained in each cc. of solution if each cc. is to represent a pound per ton of lime to be added. $0.0146068 \times 1000 = 14.6068$ grms. of oxalic acid to be added to 1 litre of water to make the standard solution.

A standard alkali solution of equal strength to the standard acid may be prepared as follows:—The reaction between oxalic acid and caustic soda is represented by $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} + 2\text{NaOH} = \text{Na}_2\text{C}_2\text{O}_4 + 3\text{H}_2\text{O}$, in which 126 parts of oxalic acid neutralise 80 parts of sodium hydroxide. The weight of sodium hydroxide which should be contained

in a litre of standard alkali is found, therefore, from the proportion—

$$126 : 80 :: 14.6068 : x \quad x = 9.274$$

In weighing out the NaOH, which is seldom pure, it is best to take, say, 9.3 grms. and dissolve in 900 cc. of distilled water, making preliminary titrations against standard acid and calculating the dilution necessary. This calculation sometimes seems to give trouble to those unfamiliar with such work, so an example will be worked out.

Suppose that it was found that 10 cc. of the alkali solution required 11.2 cc. of the standard acid; then for each 10 cc. of the alkali remaining of the 900 cc. there must be added 1.2 cc. of water; there remains 900—10 or 890 cc. The water to be added therefore equals $890 \div 10 \times 1.2$, or 106.8 cc. The alkali solution, if kept in a well-stoppered bottle, will vary but little.

To Determine Soluble Acidity.

Place 26 grms. of ore (ground to 100 mesh) in a clean, dry agitator bottle with 100 cc. of distilled water and agitate for from one-half to one hour. Allow to settle for a few minutes, then decant the clear supernatant liquid into a filter and collect the filtrate in a clean, dry beaker. (Do not wash the residue or otherwise dilute the filtrate). Measure 50 cc. of the filtrate into an Erlenmeyer flask, add a few drops of phenolphthalein, and titrate with the standard alkali solution.

Care must be taken not to over titrate, because the amount of soluble acidity in most ores is very small. If, however, this is done the solution may be titrated back with the standard acid. The number of cc. alkali used measures the amount of soluble acidity.

To Determine the Total Acidity.

Place 26 grms. of ore (100 mesh) in a clean agitator bottle with 100 cc. of standard alkali solution. Agitate for at least six hours. Allow to settle, decant the clear liquid into a filter, and collect filtrate in a clean, dry beaker. Titrate 50 cc. of the filtrate with the standard acid solution.

Fifty cc. minus the number of cc. of standard acid used equals the number of cc. of standard alkali neutralised by the total acidity of the ore, and hence the number of pounds of lime to be added per ton.

The latent acidity is found by subtracting the soluble acidity from the total acidity.—*Chemical Engineer*, xxi., No. 6.

STUDIES IN THE STEREOCHEMISTRY OF QUINIVALENT NITROGEN.*

RESOLUTION OF THE ASYMMETRIC QUATERNARY AMMONIUM COMPOUNDS.

By SHIGERU KOMATSU.

(Continued from p. 232).

B. *Lavo Methyl n-Propyl Phenyl Benzyl Ammonium Iodide*, $(\text{CH}_3)(\text{C}_3\text{H}_7)(\text{C}_6\text{H}_5)(\text{C}_7\text{H}_7)\text{NI}$.

ADDING a potassium iodide solution to an aqueous solution of pure dextro methyl *n*-propyl phenyl benzyl ammonium dextro-bromocamphorsulphonate, white crystalline precipitate of *lavo* methyl *n*-propyl phenyl benzyl ammonium iodide soon began to separate out; it was recrystallised from hot alcohol in a dark place with the protection of optical inversion by the sunlight. The platy crystals thus obtained were soluble in alcohol and acetone, and most easily in chloroform, and melted at 146° to 147° .

The analysis and determinations of the rotatory power of the substance were made, and the results will be shown as follows:—

* *Memoirs of the College of Science, Kyoto Imperial University*, 1915, i., No. 3.

0.2481 grm. of this substance gave 0.1592 grm. AgI.

Iodine calculated for $C_{17}H_{22}NI$ 34.62

Iodine found 34.68

(a). A solution of 0.991 grm. iodide made up to 25 cc. with alcohol at 25°, gave $\alpha_D^{25} = -0.68^\circ$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -93.31^\circ$.

(b). A solution of 0.1028 grm. iodide made up to 25 cc. with alcohol at 25°, gave $\alpha_D^{25} = -0.77^\circ$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -93.63^\circ$.

(c). A solution of 0.1016 grm. iodide made up to 25 cc. with alcohol at 25°, gave $[\alpha]_D^{25} = -0.76^\circ$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -93.51^\circ$.

Consequently, the mean specific rotatory power of the iodide is $[\alpha]_D^{25} = -93.48^\circ$.

C. *Lævo* Methyl *n*-Propyl Phenyl Benzyl Ammonium Bromide, $(CH_3)(C_3H_7)(C_6H_5)(C_7H_7)NBr$.

The substance prepared from pure dextro methyl *n*-propyl phenyl benzyl ammonium dextro-bromocamphorsulphonate and potassium iodide, crystallised in rhombic prisms from alcoholic solution. It melts at 166° to 167°, and is more soluble in organic solvents than the corresponding iodide.

The analytical result of the substance will be mentioned below.

0.2244 grm. substance gave 0.1317 grm. AgBr.

Bromine calculated for $C_{17}H_{22}NBr$ 25.00

Bromine found 24.98

The determination of the rotatory power was conducted with the purified substance, and the result is as follows:—

A solution of 0.116 grm. bromide made up to 25 cc. with alcohol at 25° gave $\alpha_D^{25} = -1.06^\circ$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -114.2^\circ$.

D. *Lævo* Methyl *n*-Propyl Phenyl Benzyl Ammonium Chloroplatinate, $[(CH_3)(C_3H_7)(C_6H_5)(C_7H_7)N.Cl]_2Pt.Cl_4$.

Lævo methyl *n*-propyl phenyl benzyl ammonium hydroxide obtained by the interaction of pure *lævo* methyl *n*-propyl phenyl benzyl ammonium iodide and moist silver oxide, was neutralised with hydrochloric acid; the ammonium chloride thus formed was converted into the double salt with platinum chloride.

The double salt re-crystallised from a large quantity of hot water was yellow fine-needle-shaped crystals, melting at 163.5° to 164°, while the corresponding inactive salt melts at 159° to 160°.

The salt, dried at 100°, was analysed and gave the following result:—

0.1824 grm. double salt gave 0.039 grm. Pt on ignition.

Platinum calculated for $C_{34}H_{44}N_2Cl_6Pt$ 22.01

Platinum found 21.49

E. *Dextro* Methyl *n*-Propyl Phenyl Benzyl Ammonium Iodide, $(CH_3)(C_3H_7)(C_6H_5)(C_7H_7)N.I$.

Evaporating the filtrate from *lævo* methyl *n*-propyl phenyl benzyl ammonium dextro-bromocamphorsulphonate, there was left a syrupy residue from which dextro methyl *n*-propyl phenyl benzyl ammonium iodide was obtained in white crystalline form. It crystallises from alcohol in white plates which melt at 146° to 147° as observed in its antipode.

The analysis of the substance gave the following result:—

0.3449 grm. substance gave 0.2182 grm. AgI.

Iodine calculated for $C_{17}H_{22}NI$ 34.62

Iodine found 34.19

(a). A solution of 0.098 grm. iodide made up to 25 cc. with alcohol at 25°, gave $\alpha_D^{25} = +0.70^\circ$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +89.28^\circ$.

(b). A solution of 0.0977 grm. iodide re-crystallised from alcohol, made up to 25 cc. with alcohol at 25°, gave $\alpha_D^{25} = +0.71^\circ$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +90.84^\circ$.

F. *Dextro* Methyl *n*-Propyl Phenyl Benzyl Ammonium Chloroplatinate, $[(CH_3)(C_3H_7)(C_6H_5)(C_7H_7)N.Cl]_2Pt.Cl_4$.

The double salt with platinum chloride prepared from dextro methyl *n*-propyl phenyl benzyl ammonium iodide by the usual method, consists of yellow fine needle-shaped crystals which melt at 163° to 164°. Its analysis gave the following result:—

0.1906 grm. of the double salt gave 0.0416 grm. Pt on ignition.

Platinum calculated for $C_{34}H_{44}N_2Cl_6Pt$ 22.01

Platinum found 21.84

5. Resolution of Methyl Allyl Phenyl Benzyl Ammonium Iodide into its Optically Active Components.

A. α -Methyl Allyl Phenyl Benzyl Ammonium Dextro-bromocamphorsulphonate,



α -Methyl allyl phenyl benzyl ammonium iodide prepared from methyl benzyl aniline and allyl iodide, was boiled with an equi-molecular silver dextro-bromocamphorsulphonate in an acetone-ethyl acetate solution on a water-bath for two hours.

By the re-crystallisation of the reaction product three times from acetone, α -methyl allyl phenyl benzyl ammonium dextro-bromocamphorsulphonate was obtained in white plates which melt at 133° to 134°.

It is soluble in acetone, ethyl acetate, alcohol, and water, dried at 100° it was analysed:—

0.2054 grm. substance gave 0.082 grm. BaSO₄.

Sulphur calculated for $C_{27}H_{34}O_4NSBr$ 5.84

Sulphur found 5.48

(a). A solution of 0.94 grm. of the substance made up to 25 cc. with water at 25°, gave $\alpha_D^{25} = +3.86^\circ$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +51.33^\circ$.

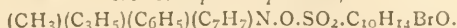
(b). A solution of 0.8142 grm. of the substance re-crystallised from acetone, made up to 25 cc. with water at 25°, gave $\alpha_D^{25} = +3.36^\circ$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +51.56^\circ$.

(c). A solution of 0.3493 grm. of the substance (the Sample *b* re-crystallised three times from ethyl acetate) made up to 25 cc. with water at 25°, gave $\alpha_D^{25} = +1.37^\circ$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +49.63^\circ$.

(d). A solution of 0.263 grm. of the substance (the Sample *c* re-crystallised four times from ethyl acetate) made up to 25 cc. with water at 25°, gave $\alpha_D^{25} = +1.10^\circ$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +52.28^\circ$.

The ammonium iodide derived from the ammonium bromocamphorsulphonate was observed to be optically inactive.

B. γ -Methyl Allyl Phenyl Benzyl Ammonium Dextro-bromocamphorsulphonate,



By the interaction of γ methyl allyl phenyl benzyl ammonium iodide, prepared from methyl allyl aniline and benzyl iodide, and silver dextro-bromocamphorsulphonate, γ -methyl allyl phenyl benzyl ammonium dextro-bromocamphorsulphonate was obtained, which crystallises in white crystals from acetone. It melts at 135° to 136°, and its analysis gave the following result:—

0.2251 grm. of the substance gave 0.0941 grm. BaSO₄.

Sulphur calculated for $C_{27}H_{34}O_4NSBr$ 5.84

Sulphur found 5.74

The optical measurement of two preparations, *a* and *b*, was conducted, and the results are as follows:—

(a). A solution of 1.0086 grm. of the substance made up to 25 cc. with water at 25°, gave $\alpha_D^{25} = +4.01^\circ$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +50.81^\circ$.

(b). A solution of 0.7699 grm. of the substance obtained by the crystallisation of the preparation *a*, made up to 25 cc. with water at 25°, gave $\alpha_D^{25} = +3.25^\circ$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +52.77^\circ$.

(To be continued).

RADIOMETRIC MEASUREMENTS OF THE
IONISATION CONSTANTS OF INDICATORS.*

By E. J. SCHAEFFER, M. G. PAULUS, and HARRY C. JONES.

(Continued from p. 233).

Results with Methyl-orange.—The hydrolysis and ionisation constants for methyl-orange, recorded in Tables V. and VII., are to be regarded as part of the preliminary work. Table IV. contains the percentage transmissions for nine solutions of methyl-orange prepared in accordance with the scheme given below. The concentration of the mother-solutions of methyl-orange was 3.973×10^{-4} ; that of the mother-solution of sulphuric acid 3.0885×10^{-4} grm.-molecules per litre.

Attention is called to the blank spaces appearing in some of the tables. For some solutions and certain wave-lengths of light no transmission values were obtained. It was known at the time the measurements were made that certain transmission values were erroneous, due either to variations in the current intensity or to vibrational disturbances. The action of light, as has been previously explained, renders these solutions of methyl-orange more transparent, and for this reason it was necessary to complete the reading as soon as possible. This excluded the possibility of re-measuring the percentage transmissions made when conditions were unfavourable for accurate readings.

Table V. gives the quinoid salt and azo-base concentrations of each of the above solutions, the hydrolysis constant (K_w/K_i), and the ionisation constant K_i of methyl-orange as a base.

TABLE V.

Solution.	$\lambda =$ A.U.	Azo-base. $c' \times 10^4$.	Quinoid salt. $c \times 10^4$.	$K_w/K_i \times 10^4$.	$K_i \times 10^{11}$.
II.	5798	1.91	0.353	6.5	1.3
III.	5748	1.84	0.716	6.1	1.3
	5797	1.80	0.897	4.4	1.8
	5847	1.82	0.813	5.1	1.6
IV.	5748	1.75	1.16	5.2	1.6
	5797	1.69	1.46	3.7	2.2
	5847	1.74	1.23	4.8	1.7
V.	5748	1.64	1.69	4.4	1.9
	5797	1.63	1.78	4.0	2.0
	5847	1.65	1.68	4.4	1.8
VI.	5748	1.50	2.41	4.5	1.8
	5797	1.46	2.61	3.9	2.0
	5847	1.43	2.76	3.5	2.3
VII.	5847	1.46	2.62	4.6	1.8
	5797	1.46	2.65	4.5	1.8

Averages.. . . . 4.5×10^{-4} 1.8×10^{-11}

The calculations of the hydrolysis and ionisation constants are based on logarithmic functions; and where the transmission of the solution is nearly complete, a slight variation from the actual percentage transmission will cause a great change in the calculated hydrolysis and ionisation constants. If we consider an experimental case where the amount of absorption to be measured is slight, the above can be made quite clear. Solution II. in Table IV. for wave-length of light $\lambda = 5798$ A.U. actually gave a percentage transmission of 85.6. Changing the percentage transmission by small amounts, and calculating the value of the hydrolysis and ionisation constants from these values, we obtain:—

$1/10$.	K_w/K_i	K_i
85.6	6.46×10^{-4}	1.25×10^{-11} (a)
86.0	7.21 "	1.12 "
86.6	8.59 "	0.94 "

(a) Found experimentally.

It will thus be seen that changing the percentage transmission by about 1 per cent will cause a variation in the ionisation constant of about 25 per cent. When conditions are not satisfactory, it is quite possible that the error in some of the percentage transmissions may be greater than 1 per cent. Considering these facts, the constants show that the efforts which were made to eliminate errors arising from variations of the current intensity and vibrational disturbances were fairly successful.

TABLE VII.

Solution.	$\lambda =$ A.U.	Azo-base. $c' \times 10^4$.	Quinoid salt. $c \times 10^4$.	$K_w/K_i \times 10^4$.	$K_i \times 10^{11}$.
IV.	5698	8.30	8.14	5.5	1.5
	5723	8.55	6.88	6.8	1.2
	5748	8.41	7.62	6.0	1.4
	5773	8.49	7.18	6.4	1.3
	5797	8.42	7.56	6.0	1.4
	5823	8.22	8.56	5.1	1.6
	5847	8.06	9.36	4.5	1.8
III.	5698	8.42	7.58	4.3	1.9
	5723	8.72	6.03	5.8	1.4
	5748	8.78	5.76	6.2	1.3
	5773	8.55	6.88	4.9	1.7
	5797	8.54	6.95	4.8	1.7
	5823	8.40	7.63	4.3	1.9
II.	5698	9.04	4.47	5.3	1.5
	5723	9.28	3.24	7.9	1.0
	5748	9.22	3.53	7.1	1.1
	5797	9.20	3.62	6.9	1.2
	5823	9.28	3.22	8.0	1.0
	5847	8.96	4.84	4.8	1.7

Averages.. . . . 5.8×10^{-4} 1.5×10^{-11}

TABLE IX.

Solution.	$\lambda =$ A.U.	Azo-base. $c' \times 10^4$.	Quinoid salt. $c \times 10^4$.	$K_w/K_i \times 10^4$.	$K_i \times 10^{11}$.
VI.	5797	0.975	2.76	3.4	2.4
	5848	0.975	2.76	3.4	2.4
V.	5723	1.193	1.67	4.3	1.9
	5748	1.147	1.99	3.5	2.3
	5773	1.167	1.80	3.8	2.1
	5797	1.203	1.62	4.5	1.8
	5898	1.197	1.65	4.4	1.8
IV.	5723	1.211	1.58	3.5	2.3
	5748	1.211	1.58	3.5	2.3
	5773	1.227	1.50	3.8	2.1
	5798	1.235	1.46	4.0	2.0
	5848	1.315	1.36	4.7	1.8
	5898	1.245	1.42	4.2	1.9
III.	5723	1.281	1.23	3.5	2.3
	5748	1.277	1.25	3.5	2.3
	5773	1.295	1.16	3.9	2.1
	5798	1.269	1.24	3.5	2.3
	5848	1.309	1.09	4.3	1.9
	5898	1.301	1.13	4.0	2.0
II.	5723	1.372	0.773	4.1	2.0
	5748	1.390	0.687	4.9	1.7
	5848	1.383	0.718	4.6	1.8

Averages.. . . . 4.0×10^{-4} 2.1×10^{-11} * From the *Journal of the American Chemical Society*, xxxvii., No. 4.

TABLE IV.

 (I/I_0 for depth of solution = 20 mm.).

Solution I. 50 cc. methyl-orange diluted to 100 cc.										
" II. 50 " 5 cc. sulphuric acid, diluted to 100 cc.										
" III. 50 " 10 " " "										
" IV. 50 " 15 " " "										
" V. 50 " 20 " " "										
" VI. 50 " 30.9 " " "										
" VII. 50 " 35 " " "										
" VIII. 50 " 1 cc. concentrated sulphuric acid, diluted to 100 cc.										
" IX. 50 " 2 " " "										
$\lambda = A.U.$	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	Average of VIII. and IX.
5748	84.6	—	71.9	65.1	57.7	49.1	46.7	9.5	8.4	8.95
5798	90.0	85.6	79.3	73.3	70.0	62.2	61.0	22.1	22.1	22.1
5847	91.4	—	84.6	81.4	77.9	70.3	—	35.7	35.7	35.7

TABLE VI.

 (I/I_0 for depth of solution = 20 mm.).

Solution I. 50 cc. methyl-orange diluted to 100 cc.									
" II. 50 " 10 cc. sulphuric acid, diluted to 100 cc.									
" III. 50 " 15 " " "									
" IV. 50 " 20 " " "									
" V. 50 " 1 cc. concentrated sulphuric acid, diluted to 100 cc.									
" VI. 50 " 0.5 " " "									
" VII. 50 " 0.2 " " "									
" VIII. 50 " 0.5 " " "									
$\lambda = A.U.$	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	Average of V., VI., VII., and VIII.
5698	87.7	75.3	67.6	66.3	16.6	15.2	15.2	17.1	16.0
5723	88.9	80.7	74.2	72.3	20.1	20.1	20.2	—	20.1
5748	90.3	83.7	79.8	76.6	31.9	31.2	30.7	30.3	31.3
5773	91.6	—	81.7	81.3	38.8	39.0	39.5	41.1	39.9
5797	93.5	88.9	85.1	84.4	48.1	49.2	48.7	47.5	48.4
5823	94.5	91.3	87.0	86.2	55.3	53.8	55.0	56.4	55.1
5847	95.6	91.7	—	88.2	63.2	62.6	61.4	61.7	62.2

TABLE VIII.

 (I/I_0 for depth of solution = 20 mm. Temperature = 20°).

Solution I. 50 cc. methyl-orange diluted to 100 cc.									
" II. 50 " 10 cc. sulphuric acid, diluted to 100 cc.									
" III. 50 " 15 " " "									
" IV. 50 " 20 " " "									
" V. 50 " 25 " " "									
" VI. 50 " 40 " " "									
" VII. 50 " 0.7 cc. concentrated sulphuric acid, diluted to 100 cc.									
" VIII. 50 " 0.8 " " "									
$\lambda = A.U.$	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	Average VII. and VIII.
5723	88.2	71.8	63.7	58.0	51.6	—	11.8	11.6	11.7
5748	90.0	77.6	68.6	64.0	59.8	—	17.1	17.6	17.4
5773	91.6	—	75.2	71.0	67.4	—	24.8	24.9	24.9
5797	93.4	—	78.7	76.2	72.6	63.8	32.5	33.2	32.4
5848	95.4	89.6	86.6	84.5	—	75.2	49.0	49.8	49.4
5898	97.2	—	91.4	89.8	88.7	—	63.5	63.5	63.5

The transmission values given in Table VI. are for a much more dilute solution of methyl orange. The concentration of the mother-solution of methyl-orange was 1.9865×10^{-4} grm.-molecules per litre; that of the mother solution of sulphuric acid being 3.0885×10^{-4} grm.-molecules per litre.

The constants given in Table VII. are calculated from the values in Table VI.

The ionisation constants for methyl-orange, recorded in Tables V. and VII., do not by any means represent the most accurate values that can be obtained by this radiometric method. It is necessary that the measurements be made in a region of the spectrum where the light energy is not intense, and, consequently, the deflections of the radiometer are small. The largest deflection that could be obtained for wave-lengths of light $\lambda = 0.58 \mu$ was 60 mm. It is for this reason that vibrations (and variations in the

intensity of the Nernst glower) seriously interfere with the accuracy of the percentage transmissions. The temperature which prevailed at the time these measurements were made was not accurately known. However, it is certain that it was between 20° and 23°. The constants were calculated for 20°; therefore there is good reason to suppose that the real constants are somewhat higher (see Table IX.).

The transmission values given in Table VIII. were obtained when the temperature at the time of measurement was known to be 20°. The measurements were made at night, when the building was fairly free from vibrations. Under these conditions the scale could be read accurately to 0.25 mm. Except for Solutions II. and VI., the current intensity remained very constant. A different mother-solution of methyl-orange was used, its concentration being 3.054×10^{-4} grm.-molecules per litre. The con-

centration of the mother-solution of sulphuric acid was 3.089×10^{-4} gm.-molecules per litre.

The values calculated from Table VIII. are recorded in Table IX.

The greatest variation from the mean is less than 20 per cent. It has already been shown in one experimental case that an error of 1 per cent in the percentage transmission would cause a variation of 25 per cent in the ionisation constant. The determination of the percentage transmissions from which the constants recorded in Table IX. are calculated was made under the most favourable conditions. These constants therefore more likely represent the true constants of the indicator.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, October 22, 1915.

Dr. A. RUSSELL, M.A., Vice-President, in the Chair.

A PAPER entitled "*The Radiation and Convection from a Heated Wire in an Enclosure of Air*" was read by Dr. T. BARRATT.

The object of the experiments here recorded was to determine the numerical relation between the radiation and the convection losses from a heated metallic wire or rod placed in a gas at constant temperature. The method consisted in (1) measuring the amount of heat required to maintain the temperature of the wire a given amount (about 10° C.) above that of the surrounding gas, the surface of the wire being (a) coated with a dead-black varnish, (b) uncoated, (2) comparing the radiations from two surfaces exactly similar to (a) and (b) by means of a thermopile.

It is shown that if the total heat lost from unit surface of the wire is a times greater from a "black" wire than from a "bare" one, while the radiation from the black surface is b times more than that from the unblackened surface, then—

$$\frac{r_2}{c} = \frac{a-b}{a-1}, \text{ and } \frac{r_1}{c} = \frac{b(a-b)}{a-1};$$

where r_2 , r_1 , are the radiations from "black" and "bare" surfaces respectively and c is the convection.

The experiments indicate that of 100 parts of "total heat" lost from a wire at air temperatures, 2.5 consist of radiation for a bare wire, and 12.6 for a "black" wire. At 100° C., these percentages become 4.4 and 20.7 respectively.

DISCUSSION.

Dr. H. BORNES asked if the author had tested the validity of the assumption that the convection was independent of the nature of the surface of the wire.

Mr. F. E. SMITH asked why the platinum thermometer employed to give the temperature of the enclosure was placed inside it. There would be a temperature gradient between the wire and the enclosure and the thermometer could not give the correct temperature of the latter.

Dr. W. ECCLES asked if the size of the enclosure affected the results. He had once studied the effects of convection in lifting the boom of a small micro-balance. The convection was due to the heating effect of the current in the instrument and the magnitude of the effect depended on the size of the enclosure.

Dr. A. RUSSELL welcomed the author's work as being the first experimental attempt to determine the proportion of heat lost by radiation and convection. In early discussions on the heating of cables prominence was given to the nature of the surface which they should have to make the radiation as great as possible. It appeared from the author's results that practically all the heat was lost by

convection and so the surface was not of much consequence. With different diameters of wire did the convection loss vary as the square root of the diameter? It should do so if the currents were uniform. Did the amount of heat radiated per unit depend on the curvature? From the results it seemed to decrease as the radius was increased.

Mr. J. H. BRINKWORTH (communicated remarks) referred to some results of his experiments by the continuous flow method on the specific heat of steam (*Phil. Trans.*, A. 535, pp. 434 and 436). In these measurements the heat loss from the calorimeter was varied by altering the pressure of the air in the sheath surrounding the flow tube. The heat loss per degree per centimetre length of flow tube, when the sheath was evacuated as perfectly as possible—in which case radiation alone occurred—lies between 5 and 10 per cent of the loss when the pressure in the sheath was about 1 mm. of mercury.

Dr. BARRATT, in reply, said that he did not quite see how to verify experimentally that the convection was the same with the two kinds of surface employed. He thought that if the surface was smooth in each case the convection loss was bound to be the same. With regard to the position of the second platinum thermometer he had found that when it was placed about half-way along and below the wire the temperature was always accurately the same as that of the enclosure. He had taken temperatures at various parts of the enclosure from which he had concluded that the convection currents were quite regular. He had not tried different sized enclosures. With wires of different diameters the total heat loss per square centimetre decreased as the diameter of the wire increased, but he had not seen whether or not the square root law mentioned by the Chairman held for the convection loss.

A paper "*On the Determination, by the Method of Diffusive Convection, of the Coefficient of Diffusion of a Salt Dissolved in Water*," was read by Dr. A. GRIFFITHS.

In general the diffusion of matter like the diffusion of heat produces convective currents, and there is a diffusive convection which is akin to thermal convection. In the apparatus described in the paper the convective flow is of the order of one millionth of a cubic centimetre per second from the top of one set of diffusion tubes to the top of another set. The top of each set of diffusion tubes is enclosed in a glass vessel containing water, and the one vessel is connected to the other by means of a long capillary tube. Each set of eight diffusion tubes is of length about 5 cm., and has a total area of cross-section of about 0.5 sq. cm. The capillary tube is about 150 cm. long, and has a diameter of about 1 mm.; and the linear flow of a coloured index, consisting of a feeble solution of uranine, is of the order of 10 cm. per day. The index is introduced by means of a special four-way glass tap.

DISCUSSION.

Mr. B. W. CLACK said he had repeated his experiments under all possible conditions to try to locate the cause of the 6 per cent. difference between his results and those of the author, but so far without success. In the author's arrangement the water was inside the tube and the solution was in the tank. He had tried that with his apparatus but gave it up in 1908 in favour of having the water in the tank and the solution inside. He showed some curves taken with the two arrangements. In the case of dilute solutions the results were the same, but with strong solutions there was about 4 per cent. difference. It may be in this direction that the explanation of the discrepancy has to be looked for.

Mr. T. BARRATT asked if the introduction of a salt to prevent the formation of fungoid growths would not be likely to cause some error.

Dr. GRIFFITHS replied that the amount of copper chloride introduced was exceedingly small, about 1 cubic cc. of 20 per cent solution being added to the liquid in question, and he did not think it could produce any appreciable error.

A paper entitled "*The Magnitude of the Thermal Resistance Introduced at the Slightly Conical Junction of Two Solids and its Variation with the Nature of the Surfaces in Contact*," by Dr. T. BARRATT, was taken as read.

The abrupt fall of temperature caused by the thermal resistance at the slightly conical junction of two solids has been examined, the method consisting in constructing a "double joint," thus doubling also the thermal resistance effect.

In the case of wires of small diameter, the fall of temperature was found to be $2\frac{1}{2}$ per cent; that is, the temperature of the "hot" end of the wire is $2\frac{1}{2}$ per cent lower than that of the copper block into which the end of the wire was fitted.

This percentage fall of temperature is practically the same at all temperatures of the enclosure (up to $100^{\circ}\text{C}.$), and is independent of the excess of temperature of the end of the wire above that of the enclosure at any rate, up to $10^{\circ}\text{C}.$ or $12^{\circ}\text{C}.$

For wires of greater diameter (6 mm.) the resistance is rather less than for smaller wires.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, November 3, 1915.

Mr. A. CHASTON CHAPMAN, President, in the Chair.

PROFS. Arthur William Crossley, Herbert Jackson, James Charles Philip, William Jackson Pope, and Messrs. Daniel James Davies, Martin Oislow Forster, Frederick Ion Richardson, and George Henry Warburton were elected Members of the Society.

Certificates were read for the first time in favour of Messrs. Thomas Featherstone Harvey, 69, North Road, West Bridgford, Nottingham; Cyril Herbert Manley, 292, Ifley Road, Oxford; Caryl Cameron Roberts, Watling Chambers, Canterbury; and Frank Thomas Shutt, Experimental Farm, Ottawa, Canada.

Certificates were read for the second time in favour of Messrs. Eric Keightley Rideal, 28, Victoria Street, Westminster; and Arthur Sidney Carlos, 42, Foxley Road, N. Brixton, S.W.

The following papers were read:—

"*Formic Acid as a Reagent in Essential Oil Analysis*." By W. H. SIMMONS, B.Sc.

Continuing his work on the determination of citronellol in geranium oils by formylation ("Year Book of Pharmacy," 1913) the author has examined fifty further samples of Bourbon geranium oil, including most of the more important brands, and finds them to contain 45 to 57 per cent of citronellol, while another ten samples of African geranium oil gave only 32 to 43 per cent, thus confirming the previous results. Experiments on the formylation of various essential oils and their alcoholic constituents shows that terpineol is almost completely decomposed by the process, geraniol and linalol are both converted into an appreciable quantity of ester, santalol is only very partially decomposed, and citronellol, menthol, and the borneol in rosemary oil may be approximately estimated by the process. It is hoped by further experiment, suitably modifying the strength and proportion of acid and possibly duration of heating, to establish a formylation process for determination of menthol in peppermint oils, which may take the place of the acetylation process, over which formylation offers distinct advantages.

"*Melting-Point of Salicylic Acid and a Test for the Presence of Parahydroxybenzoic Acid*." By HENRY L. SMITH, B.Sc., F.I.C.

The melting-point of carefully purified salicylic acid after drying over sulphuric acid is $158.5^{\circ}\text{C}.$ The presence of small amounts of parahydroxybenzoic acid appreciably lowers the melting-point.

The crystalline forms of the acids are different and the presence of parahydroxybenzoic acid may be detected by means of the microscope.

"*Persistence of Hydrogen Peroxide in Milk*." By EDWARD HINKS, B.Sc., F.I.C.

Experimental results were given showing that unqualified statements as to the length of time during which hydrogen peroxide will persist in milk are of no value. The length of time depends upon the age and condition of the milk. In a case in which peroxide was added to a perfectly fresh milk in the proportion of 0.2 per cent, it was still present in estimable proportion after the lapse of 18 months. It was found that within the range of from 15° to $37^{\circ}\text{C}.$ the higher the temperature the longer did the peroxide persist. The peroxidase reactions were also studied concurrently with the peroxide determinations.

FARADAY SOCIETY.

Annual General Meeting, October 19, 1915.

THE following Officers and Members of Council were elected to serve for the year 1915-16:—

President—Sir Robert Hadfield, F.R.S.

Vice-Presidents—Prof. K. Birkeland; Bertram Blount; W. R. Bousfield, K.C.; Prof. F. G. Donnan, F.R.S.; Dr. Eugene Haanel; Prof. A. K. Huntington; Dr. T. Martin Lowry, F.R.S.

Treasurer—F. Mollwo Perkin, Ph.D.

Council—W. R. Cooper; Dr. C. H. Desch; Dr. J. A. Harker, F.R.S.; Emil Hatschek; Cosmo Johns; Prof. Alfred W. Porter, F.R.S.; E. H. Rayner; A. Gordon Salamon; Dr. George Senter; Cav. Magg. E. Stassano.

The Report of the Council states that although the Society's activities have been seriously affected by the war, it was found possible to hold four meetings in the period under review, at which 27 papers were read. At one of these meetings Sir Robert Hadfield delivered his Presidential Address on "Advances in the Metallurgy of Iron and Steel," at another Mr. Charles R. Darling exhibited a very full display of the most recent types of Recording Pyrometers, which attracted much interest. The remaining meetings took the form of General Discussions, the subject of one being "Optical Rotatory Action," and the other "The Hardening of Metals." Both of these discussions were very largely attended and were most successful. They were international in character, and resulted in no less than 96 and 88 pages of contributions respectively from most of the leading authorities on the subjects.

Ordinary Meeting, October 19, 1915.

The meeting was devoted to a General Discussion on "*The Transformations of Pure Iron*," and it was presided over by Sir ROBERT HADFIELD, F.R.S., President, who introduced the subject under discussion. (See p. 206).

Dr. A. E. OXLEY University of (Sheffield) contributed the opening Paper to the Discussion. (See p. 205).

Mr. F. C. THOMPSON (Sheffield) contributed a Paper to the Discussion in which he arrived at the following conclusions:—

1. Sudden changes in the directions of one or more curves showing the relationship of the physical properties of iron to temperature, indicate with certainty the existence of α , β , γ , and δ iron with change-points at $768^{\circ}\text{C}.$, $900^{\circ}\text{C}.$, and $1400^{\circ}\text{C}.$, while another slight change has been detected magnetically and dilatometrically at about $830^{\circ}\text{C}.$

2. The A_3 point in iron taken as typical of all the changes is shown to obey the same laws as hold for other acknowledged allotropic transformations.

3. Magnetic evidence is available that the molecule of δ iron is Fe_3 , of γ iron Fe_2 , and of α iron Fe .

4. A distinct mode of packing of the α , the β , and the γ molecules is indicated crystallographically.

5. Thermally it may be shown that the changes occurring in iron are of the same nature as those which occur in other cases of allotropy in metals, *e.g.*, tin and cadmium, and also as in the case of the change from rhombic to monoclinic sulphur.

The author is therefore strongly of the opinion that the transformations in iron are essentially allotropic. At the same time he dissociates himself entirely from the view that to any of the allotropic forms *per se* is the hardness of hardened steel due. Some of the modifications will dissolve carbon as Fe_3C and some to all intents will not; but in this fact alone does the allotropy of iron bear on the constitution of steel. Whether iron is allotropic or not, it is to the solution of Fe_3C that the characteristic properties of hardened steels must be ascribed. The views of Arnold expressed in 1895 are essentially accepted to-day by the majority of metallographers, and the "hard β iron" to which the strength of hardened steel was due according to the allotropic school is dead.

Prof. PIERRE WEISS (Paris), in a communication which was read to the meeting, referred to his recent work on the magnetisation of iron at different temperatures, by which, through adopting newer values for the Curie constant, he has shown that there are at least three transformations in iron: the A_2 , which has a physical character, the A_3 , which presents a discontinuity in the susceptibility, and a third transformation in the β region, pointing to the existence of a β_1 iron with 12 magnetons and a β_2 iron with 10 magnetons in the atom. The latter change is intra-atomic and not—adopting Dr. Oxley's definition—allotropic.

M. H. LE CHATELIER (Paris) also sent a communication to the Discussion, in which he deprecated giving a new definition to the word "allotropy." Two allotropic states were merely two clearly defined states of the same composition presenting discontinuity (Benedicks), but co-existing at the same temperature and pressure. Thus fusion and vaporisation could be classed as allotropic transformations, and equally so could the A_3 and even the A_2 transformation in iron.

Prof. FREDERICK SODDY, F.R.S. (Glasgow), in his communication, referred to the work of the Braggs on crystalline structure, which showed that the conception of a molecule has no meaning as applied to a solid, because the atoms of the solid are anchored and do not exist in freely moving groups; *i.e.*, molecules at all. Oxygen and ozone seem to be the only allotropes that survive gasification. There is little evidence that sulphur and phosphorus, or still less that the metals, behave in an analogous way.

Mr. J. E. STEAD, F.R.S. (Middlesbrough), in a written communication, considered that a new definition of allotropy was called for after the work of the chemical crystallographers, and they had to consider whether the new definition was not open to criticism. Could Dr. Oxley explain in his own terms the breaking-up of large crystals of iron into small ones when they are heated through the A_3 range? There must be a profound internal physical breaking down and rebuilding of the crystalline structure, accompanied by an absorption of heat.

Prof. THOMAS TURNER (Birmingham) (communicated) did not think that to regard changes in iron as more allied to change of physical state than to true allotropy interfered with the view that there are three distinct phases in solid iron, each possessing characteristic properties.

Dr. CECIL H. DESCH (Glasgow) (communicated) discussed the bearing of "dynamic allotropy" and allotropic change as defined in a narrower sense by Honda ("a change in a substance from one phase to another at a definite temperature") on the problem of the transformations in iron. From a purely chemical point of view γ iron and the modification into which it changes on passing through A_3 are distinct phases. He agreed with Dr. Stead as to the complete decrystallisation at the A_3

point. Dr. Oxley's thermal comparisons were open to criticism as the latent heats of fusion were expressed in *grm.-calories per grm. of metal*, while the thermal evolutions accompanying allotropic and isomeric changes were given in *grm.-calories per grm.-molecule*. The correction considerably reduces the disproportion suggested. The heat evolution accompanying the change from grey to white tin, which is certainly allotropic, is 1133 *grm.-calories*, which is less than the latent heat. Moreover, the evolution of heat in iron, apart from the necessary correction, was too low as given by Dr. Oxley, for it should include the whole area of the peak in the inverse-rate in the derived differential curve. As corrected it would approximate to that for tin. He therefore concluded that there was no reason for removing the $\gamma \rightarrow \alpha$ and $\gamma \rightarrow \beta$ changes from the category of allotropic transformations.

Mr. A. McCANCE (Glasgow) (communicated) laid down the condition that a definition must be independent of a theory, and Dr. Oxley's was not so. He also dealt with the modern conception of the molecule, touched on by Prof. Soddy, and on the definite crystallisation change in iron at the A_3 point emphasised by Dr. Stead. This was something more than mere closeness of packing.

Mr. T. G. ELLIOTT (Sheffield) (communicated) thought that Dr. Oxley's test of allotropy, involving the withdrawal of restraining forces, demanded a hypothetical condition in the material to be tested. Could crystals be built up of distorted molecules?

The PRESIDENT pointed out that a knowledge of the transformations of iron was essential for the successful production of hardened steel. He mentioned the interesting fact that many of the iron alloys at the temperature of liquid air attained a tenacity of 160 tons per square inch.

Prof. H. C. H. CARPENTER thought it preferable to say that iron existed in one phase below and in another phase above 900° C. It was not certain that the molecule of iron was polyatomic. Judgment must be suspended until Prof. Bragg had examined a well formed crystal with the X-ray spectrometer. He did not see how cooling through A_3 could lead from a more open to a closer packed cubic system, seeing that there was an expansion during the transformation. Finally, he exhibited slides illustrating the remarkable crystallographic changes that occurred when iron of exceptional purity was heated for some time at 915° C., and then allowed to cool. Whether allotropic or not, very profound physical changes took place at the A_3 point.

Dr. J. A. HARKER, F.R.S., expressed his surprise that so little work had been done in the determination of the thermal constants of pure iron. He outlined a possible method for the determination of the latent heat of fusion. Thereupon—

The PRESIDENT offered to defray the cost of the work if it could be carried out at the National Physical Laboratory.

Prof. J. W. NICHOLSON thought the idea of a sort of atonic allotropy the really new thing in Dr. Oxley's conceptions. The fact was there were many varieties of allotropy, which needed sub-division into several groups. Bragg's work might be used in support of Dr. Oxley's hypothesis.

Prof. ALFRED W. PORTER, F.R.S., could not understand how Dr. Oxley's definition could receive practical application, as the only method of removing the restraining forces from the molecules of a substance was by vaporising it.

Dr. T. MARTIN LOWRY, F.R.S., protested against altering Berzelius's definition of allotropy, which had been in use for seventy years. If a new definition was required it should be attached to a new word. He was content to think that different modifications of iron might be made up of the same molecules arranged in different ways, but in the case of an element, such as sulphur, this would still be allotropy. Dr. Oxley's thermal data were unconvincing. He might have selected changes, such as the inter-

conversion of certain isomerides, in which the thermal changes were small.

Dr. E. K. RIDEAL referred to Partington's work on the vapour-pressure of copper sulphate crystals, carried out by the method of passing dry air over the crystals. The differences between these values and those obtained by the static method might be explained by taking into consideration the space lattices of the crystals. Similar work might be done in the case of iron.

Dr. J. R. PARTINGTON pointed out that the atomicity of metals in the solid space could be determined from measurements of specific heat. Nernst found that nearly all the metals were monatomic.

Dr. H. BORNES asked Dr. Oxley why he had ignored Weiss's recent work, which proved that iron was poly-atomic and that β iron differed from γ iron in atomicity.

Dr. A. E. OXLEY, in reply, said that Bragg's work was not necessarily opposed to his views, because Bragg himself agreed that in the case of complex molecules it was possible to draw a boundary round a certain group of atoms in a crystal and say that they belonged to a particular molecule.

The linear expansion found by Benedicks to occur in iron when it cools through the A_3 point was not opposed to a closer packing of the molecules in the direction of spontaneous magnetisation.

With regard to the definition of allotropy, it was obvious that examples of the type of oxygen and ozone should not be classed with cases which could be explained by loose molecular association.

His definition of allotropy was theoretical to a large extent, but the idea could be followed by considering the case of ozone and oxygen. In the crystalline state these substances were different from each other; on removing the restraining forces by fusion or vaporisation, they were still more different from each other and were therefore allotropes.

Weiss's work on the magnetic properties of iron was no proof either of the atomicity of the different kinds of iron or of the magneton theory, as he assumed the truth of one to prove the other.

The following Papers were taken as read :—

"The Transference of Electricity by Colloidal Particles."

By F. POWIS, M.Sc. (Leeds).

An attempt is made to calculate the charge carried by the particles of a colloidal solution produced by sparking, (1) from a modification of Stokes's formula, (2) from the increase in conductivity on making the solution. Although the data available for the calculations are not very satisfactory, the second method gives a value much greater than the first. The author believes this is because the particles are not like the ions of an electrolyte solution, but that anions and cations are adsorbed on their surface in such a way that the concentration of each gradually decreases with increasing distance from the particle, until each finally becomes equal to that in the bulk of the surrounding medium; the ions are so arranged, however, that with a negative colloid the layers nearer the particle contain an excess of anions, and those further away an excess of cations, whilst with a positive colloid this is reversed.

"Electrolysis of Nitric, Sulphuric, and Orthophosphoric Acids using a Gold Anode." By F. H. JEFFERY, M.A. (University Chemical Laboratory, Cambridge). (See p. 227).

"Electrolysis of Concentrated Hydrochloric Acid using a Copper Anode." By F. H. JEFFERY, M.A. (See p. 235).

"The Thermal Decomposition of Hydrogen Peroxide in Aqueous Solution." (Preliminary Note). By WILLIAM CLAYTON (Musparr Laboratory of Physical and Electrochemistry, the University of Liverpool). (Will be inserted in full).

CORRESPONDENCE.

"FROST BITE" IN THE TRENCHES.

To the Editor of the Chemical News.

SIR,—It is generally admitted that this condition, which proved so serious a source of suffering and loss amongst our troops last winter, was due to the defective leg wear provided by the authorities.

The puttee, which is in many respects an admirable covering, being warm, elastic, fairly impermeable, and a good protective against cold, damp, thorns, branches, and dense undergrowth, has the fatal defect—due to the means of fastening, which consists of a long inelastic tape which must be wound tightly round the leg just below the knee—of interfering with the blood circulation, especially when the material shrinks under the influence of moisture, inevitable in the trenches in winter.

Early in the spring of the present year the *Lancet* and the *British Medical Journal* called attention to this matter and invited their readers to supply a fastening that would be free from the defects of the present tape.

I devised a very simple "hook-pin" and submitted it to the Editor of the *British Medical Journal*, who wrote in the issue of June 12th :—"It appears not only completely to answer the purpose in respect of puttees, but is likely also to replace the safety pin for fixing bandages."

If this device is to prove of real value to our troops and to our wounded soldiers in the hospitals, it is essential that it should be tested as widely and thoroughly as possible and at once.

I have had a number of these hook-pins made, and will gladly send a specimen to any wearer of puttees, or to any nurse or surgeon, or to anyone interested who has a friend acting in either capacity.—I am, &c.,

C. K. RUTLAND, M.D.

83 A, Chester Square, S.W.,
November 1, 1915.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxi. No. 13, September 27, 1915.

Heterogeneity of Steels.—Henry Le Chatelier and Jules Lemoine.—Certain common steels, when examined metallographically, often exhibit an abnormal distribution of perlite, i.e., of parts rich in carbon. This perlite is grouped in parallel lines separated by spaces not coloured by reagents, as they are free from carbon. This striated structure is generally attributed to phosphorus. The metal is composed of parallel bands unequally rich in phosphorus, and the carbon is concentrated in parts containing less phosphorus. This unequal distribution of carbon is an example of the general law of the partition of a substance between two solvents. Carbon is much less soluble on warming in iron containing phosphorus than in pure iron, and at concentrations below saturation it is distributed in the ratio of the solubilities. This characteristic of the localisation of phosphorus is indirect and uncertain, and for some time search has been made for reagents which would enable phosphorus to be characterised directly and its distribution studied more easily. Of such reagents that described by Stead at a recent meeting of the Iron and Steel Institute (May, 1915) seems the most satisfactory, but the authors after studying its action suggest an improvement in it. The liquid described by Stead is a

solution in aqueous methyl alcohol of a mixture of cupric chloride and magnesium chloride. The proportion of water was not stated, and the authors find that upon it depends the sensitiveness of the reagent. The following formula is the best for attacking at 20° steels containing 0.5—1 per cent of manganese and about 0.2 per cent of silicon:—

Pure rectified methyl alcohol..	100 cc.
Water ..	18 cc.
Concentrated hydrochloric acid ..	2 cc.
Crystallised cupric chloride ..	1 grm.
Crystallised magnesium chloride ..	4 grms.

A few drops of this reagent are placed upon the polished surface of the specimen and the bands become visible to the naked eye in about a minute. The copper, or a compound of copper forming dark bands, is deposited in the regions which are less rich in phosphorus. The visibility of the bands may be increased by immersing the specimen in the liquid and connecting it with the positive pole of an accumulator, while a piece of copper wire in the liquid serves as the cathode and is connected to the other pole. The action of the reagent is complex, the cupric chloride having a double action. Like all salts of copper it yields a deposit of copper upon the iron, while at the same time, owing to its ready transformation into cuprous salt, it tends to redissolve the copper already deposited. Its action depends essentially upon the relative proportions of water and alcohol. If too little water is present it is difficult to detect the bands, while with too much water the deposition of copper is too rapid and takes place uniformly over the whole surface, so that there are no clear distinctions between the regions. The formation of these bands of variable composition is not due exclusively to phosphorus. In the absence of phosphorus they may be caused by other substances such as silicon, manganese, nickel, or chromium, which are soluble in ferrite and incapable of or very slow in diffusing.

Bulletin de la Société Chimique de France.
Vol. xvii.-xviii., No. 10, 1915.

Nitration of *m*-Diethyl-phenetidine. — Frédéric Reverdin.—The author has already described the nitration of *m*-dimethyl-phenetidine, and in this paper gives the results obtained on nitrating the corresponding diethyl compound. He obtained the base by the action of ethyl bromide in slight excess on *m*-phenetidine, the mixture being heated on the water-bath for two hours. The base is a colourless oil, turning brown under the action of air and light, having a characteristic odour, miscible in all proportions with acetic acid and alcohol, distilling at 286°. When the base is dissolved in acetic acid and treated with nitric acid, being meanwhile cooled with a mixture of ice and salt, the 4.6 dinitro compound is obtained. If this is heated on the water-bath to about 65—70°, when nitrous fumes begin to be evolved, the monomethylamino ethoxybenzene derivative, *i.e.*, $C_6H_2.OC_2H_5(NO_2)_2NHC_2H_5$,
(1) (4.6) (3)

is obtained. The author has not succeeded in isolating an analysable quantity of the corresponding nitroso derivative. When *m*-diethyl phenetidine is nitrated in acetic anhydride solution the temperature rapidly rises to about 60° or 70°, even if a freezing mixture is used, and the product is $C_6H_2.OC_2H_5(NO_2)_2NC_2H_5NO_2$. When this
(1) (4.6) (3)

is heated with a 10 per cent alcoholic solution of caustic potash it yields 4.6 dinitro, 3 ethylamino, 1 phenol. There is thus no essential difference in the results of the nitration of the methyl and ethyl compounds, but in the latter case the yields are considerably less; large proportions of secondary oily products are formed, from which it is difficult to get impossible to obtain a crystalline product. The nitration derivatives of the diethyl base fuse at very much lower temperatures than those of the dimethyl base.

No. 11. 1915.

Action of SO_2 on Eserine, Geneserine, and their Derivatives.—Max Polonovski and Charles Nitzberg.—When SO_2 acts on eserine in solution variations in the polarimetric deviations are observed, and in all probability an unstable hydro-sulphono addition product is formed. With derivatives of eserine the SO_2 first neutralises the base, giving a sulphite, and then gives a coloured addition product, which is stable only in the liquid and decomposes when the excess of sulphurous gas is driven off. In the geneserine series SO_2 produces eserinic derivatives with simultaneous formation of hydro-sulphono compounds. The polarimetric deviations indicate the formation of a third compound of unknown rotatory power.

Determination of Small Quantities of Silver by Cyanimetry.—G. Rebière.—The cyanimetric method of Denigès applied to the determination of silver makes use of the formation of a precipitate of silver iodide in an ammoniacal medium in which it is insoluble, as indicating the end of the reaction between the dissolved silver salt and potassium cyanide. When centinormal solutions are used it is impossible to detect the end of the reaction by the characteristic opalescence of silver iodide, for at this dilution it requires several drops of silver nitrate solution to make it clearly visible. The author has obviated this difficulty as follows. The silver iodide appears in the colloidal state, and may easily be rendered visible by employing the property of colloids of diffusing light. The reaction is carried out in the dark, and a ray of light is passed through the vessel in which it is taking place. Tyndall's phenomenon then occurs, and the passage of the ray is marked by a bluish opalescence. Any source of light provided with a convergent lens will do for the purpose.

Solubility of Silver Oxide in Water.—G. Rebière.—The author prepared four specimens of silver oxide by the following methods:—(i). Action of pure soda upon silver nitrate in dilute solution. (ii). Action of baryta water on silver nitrate. (iii). Action of concentrated soda on recently precipitated moist silver chloride. (iv). Action of concentrated soda on recently precipitated moist silver carbonate. The first two specimens were brown and the others black; the first two were less dense than the others. Their solubilities were determined at 25° and 50° and compared. The results were all of the same order of magnitude and were very close to one another. However, they depend upon the origin of the specimen. The value found for the first specimen at 25°, *viz.*, 21.6×10^{-4} mol. grms. in 1000 cc., agrees exactly with that given by Böttger and Noyes for silver oxide prepared in the same way.

MEETINGS FOR THE WEEK.

TUESDAY, 16th.—Institution of Petroleum Technologists, 8. "The Viscosity of Oil in Relation to its Rate of Flow through Pipes," by R. T. Glazebrook, W. F. Higgins, and J. R. Pannell.

WEDNESDAY, 17th.—Microscopical, 8. "The Foraminifera of the Shore Sands and Shallow Water Zone of the South Coast of Cornwall," by E. Heron-Alden and A. Earland.

THURSDAY, 18th.—Royal Society. "Theory of the Capillary Tube," by Lord Rayleigh. "Effect of the Form of the Transverse Section on the Resistance to the Motion of an Elongated Body Parallel to its Length through a Fluid whose Viscosity is not Negligible," by C. H. Lees. "Method of Estimating Distances at Sea in Fog or Thick Weather" and "Method of avoiding Collision at Sea," by J. Joly. "Flow of Electricity through Dielectrics," by S. W. Richardson. "Kinetic Theory of Gaseous Viscosity and Thermal Conduction, and the Law of Distribution of Molecular Velocities in the Disturbed State," by S. Chapman. Chemical, 8.30. "The Principles of Crop Production," by E. J. Russell.

THE CHEMICAL NEWS.

VOL. CXII., No. 2921.

TRINITROLOLUENE.*

By MAURICE COPISAROW, M.Sc.,
Honorary Research Fellow,
Chemical Department, The University, Manchester.

THE manufacture of trinitrotoluene (T.N.T., trotyl or trilit) being a comparatively modern branch of the explosives industry, it may be of some interest to give an outline of the chemistry of this compound and of certain conditions required for its successful production.

All the six possible isomers of trinitrotoluene are known.

The pure article of commerce, the so-called—

M. p.	
α -T.N.T. 80.8° C.; 2.4.6 isomer (Wilbrand ¹ , Comey ² , Rintoul ³)	
β - " 112.0° C.; 2.3.4 " (Will ⁴)	
γ - " 104.0° C.; 2.4.5 " (Hepp ⁵ , Stadel ⁶)	
δ - " 137.5° C.; 3.4.5 " (Körner and Contardi ⁷)	
ϵ - " 97.2° C.; 2.3.5 " (" " "	
ζ - " 79.5° C.; 2.3.6 " (Molinari and Giua ⁷)	

It must be noted that the commercial T.N.T. is not exclusively the α -form, and is accompanied by the other modifications, produced from *m*-nitrotoluene, which constitutes about 4.5 per cent of the commercial mononitrotoluene. (Van den Arend⁸, Holleman¹⁰).

All the isomers are of practically the same value as explosives.

They may be identified by means of acetone and ammonia, with which they give deep red (α), greenish-yellow (β), blue (γ), orange-red (ζ), and rose-red (ϵ) colorations.

α -T.N.T. belongs as an explosive to the group intermediate between the highly sensitive, like nitroglycerin, and the fairly stable, not easily detonating, like ammonium nitrate. Comparing T.N.T. with picric acid, we find that whilst the latter gains an explosive, owing to its comparatively greater specific gravity and detonating power, the former scores very much by its lower melting-point, smaller sensitiveness towards moisture, and inertness as regards metallic oxides.* (Kast¹¹, Dautriche¹²).

The specific gravity of T.N.T., so important a problem in the packing of shells, is more or less solved by melting and pouring it into the shells, or, still better, by pouring it into the shells and letting it solidify under pressure or by rapid cooling (Bichel¹³, Block¹⁴).

T.N.T. is sparingly soluble in water,† easier in alcohol,‡ and very soluble in acetone, benzene, and toluene. It is fairly soluble in concentrated H_2SO_4 at $90-100^{\circ}$, from which it separates out unaltered on cooling or dilution.

T.N.T. is odourless, and when pure practically white; it colours the skin yellow, though not so strongly as picric acid.

The manufacture of T.N.T. is usually carried out in two or three stages, gradually increasing the concentration of acids (Rudeioff¹⁵, Escales¹⁶), and although a simple process in itself it is combined with numerous technical and chemical difficulties, which become apparent only in the actual manufacture on a large scale.

Whilst some of the difficulties are apparently of a purely local character and can be dealt with more or less easily by the management of the particular works, others are of

a more general character, affecting the very mechanism of the reaction.

The chief defects are:—

1. The presence of inorganic impurities in the product; and
2. The presence of organic intermediate and by-products.

The inorganic matter consists mainly of lead and iron salts introduced with the fuming sulphuric acid and by the action of the acids on the nitrating plant and its fittings. The presence of intermediate organic products is due to—

- (a) Imperfect stirring arrangement;
- (b) Concentration and ratio of acids;
- (c) Duration and temperature of reaction.

The formation of by-products is due to—

- I. Sulphonation;
- II. Oxidation; and
- III. Reduction;

brought about under the influence of—

1. Sulphuric acid;
2. Nitric acid;
3. Nitrous acid;
4. Metallic salts;
5. Concentration of acids, with special reference to their action on the plant; and
6. Working conditions, such as temperature, pressure, and duration of each particular stage of the reaction and period of contact between the reaction-products.

The colour of the used-up acids (specially of the re-used for the nitration of toluene to mononitrotoluene), varying from yellowish to dark brown, depends upon the composition of the acid, the colour being the darker the less nitric and more sulphonic acids, as well as oxidised organic matter, are present.

The analyses of two typical samples set below will illustrate this:—

Waste Acids from the Mononitrotoluene Plant, the Acids being previously used for making T.N.T. (Two-stage process).

	Yellowish acid. Filtered. (Sp. gr. 1.580).	Dark brown acid. Filtered. (Sp. gr. 1.575).
	Per cent.	Per cent.
HNO_2	0.20	0.0
HNO_3	2.05	0.0
H_2SO_4	63.46	58.0
H_2O	34.29	37.28
$R.SO_3H$ (a) ..	0.0	4.72
	100.00	100.00

(a) Calculated as toluenemonosulphonic acid.

These two examples, taken from a whole series of more or less similar cases, indicate that the connection between colour and composition is in no case of a casual character, but is closely connected with the whole mechanism of the reaction.

Dealing with the cause of variation in the composition of the used-up acids, we have to bear in mind that sulphonation could theoretically be brought about either—

- (a) by the preservation of the intermediary sulpho compounds, probably preceding the formation of nitro bodies, which may be formed by the substitution of the sulpho by nitro groups; or
- (b) by a reversible reaction taking place, *i.e.*, the nitro groups being gradually replaced by sulpho groups under the influence of a too long contact of the nitro compounds with the sulphuric acid.

Whichever of these two possibilities may actually operate, the method for the prevention of such sulphonation must be as follows:—

* β - and γ -T.N.T. accompanying the α -form react with lead oxide (Will⁴).

† 0.011 per cent at 15° C., 0.164 per cent at 100° C.

‡ 1.6 per cent at 22° C., 10.0 per cent at 53° C.

- I. Amount of nitric acid used must exceed at least by $\frac{1}{2}$ mol. the amount theoretically required for the carrying out of the nitration to a certain stage.
- II. The extent of nitration to be regulated more by the concentration of the acids and temperature of reaction than by the actual quantity of nitric acid present; and
- III. The reaction product is not to be kept in contact with the acids longer than is really necessary.

Dealing with the adventitious mineral matter in the form of metallic salts, it must be pointed out that the quantity present in the nitrating plant is subject to considerable fluctuations.

The mineral matter is derived from two sources:—

1. From the sulphuric acid, which is contaminated with lead sulphate in the lead chambers; and
2. From the action of the acids on the plant and its fittings.

A determination of lead sulphate in two average samples of mixed acid ($\text{H}_2\text{SO}_4 + \text{HNO}_3$) at one firm gave 0.19 per cent and 0.21 per cent of lead sulphate. Remembering that the ratio of the volume of acid used to that of the nitro body is at least 4 : 1, the quantity of lead salt in contact with the T. N. F. appears to be pretty considerable.

As to the action of the acids on the plant, it is rather a variable quantity, depending upon the quality of the cast-iron, concentration of acid, and working conditions, but one instance is, at any rate, known where the walls of the nitrating plant have been reduced by a quarter of an inch in thickness after six months' use.

The effect of the mineral matter on the process of manufacture is a double one:—

1. As a catalyst; and
2. As a chemical reagent.

Similar to the well-known case of mercury sulphate, (naphthalene $\rightarrow$ phthalic acid) the lead and iron salts probably promote oxidation of the main product.

The deteriorating effect of the metallic salts will become still more apparent when considered in conjunction with the influence of the acids upon the plant, in which case the metallic salts may become the source not only of loss and inconvenience but of great danger.

The acids attacking the plant generate among other gases a large proportion of hydrogen, which, as in the case of the aniline plant, reduces some of the nitro bodies. Under the working conditions the reaction does not stop at this stage, and under the influence of nitrous acid, so abundantly formed, and high temperature, the amino groups are diazotised, and we get ultimately cresols and nitro-cresols formed, the salts of which are highly explosive. Thus we may get as by-products:—

1. Trinitrobenzoic acid, and even tetranitromethane, owing to oxidation in case of overheating or pressure. The intense odour of the latter is sometimes observed in the factories, but the former, owing to its solubility, generally escapes detection,
2. Phenolic bodies, like cresols, owing to the reduction of some of the nitro bodies.
3. Sulphonic acids, when the quantity of nitric in the mixed acid is below the minimum.

Summing up the problem of the formation of by-products, we may state that in the process of manufacture of trinitrotoluene the following must be observed:—

1. The amount of nitric acid to be used must exceed at least by $\frac{1}{2}$ mol. the quantity theoretically required for the carrying out of the nitration to a certain stage.
2. The extent of nitration to be regulated more by the concentration of the acids, temperature, and duration of reaction than by the actual quantity of nitric acid present,
3. The reaction product is not to be kept in contact with the used-up acid longer than is really unavoidable.
4. The concentration of acid and material of plant to be such as to reduce their action on one another to a minimum.

5. The starting materials (toluene and acids) must be pure.

The residue from the mother-liquors consists of a complex mixture of various di- and tri-nitrotoluenes. By nitrating this with a mixed acid containing only 15 per cent of nitric acid a "liquid trinitrotoluene" is obtained, which has considerable power, and has the property of gelatinising collodion cotton, as nitroglycerin does (Nobel and Co., Hamburg¹⁷). It is used in the manufacture of gelatinised explosives. It contains 16.6 to 17.2 per cent of nitrogen, whereas pure trinitrotoluene contains 18.5 per cent and dinitrotoluene 15.4 per cent (Marshall¹⁸).

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INTRODUCTION TO THE THEORY OF RELATIVITY.

By F. H. LORING.

(Continued from p. 237).

The establishment of time by light signals is easier to comprehend if we take three typical examples and illustrate them diagrammatically. Let E and M represent respectively the earth and moon, which we will individualise and provide with watches to shorten the description. The large arrow represents their direction of movement through space, and to simplify matters, the movements will be along straight lines, and wide departures from actuality (as in Fig. 6) will be made in order to have the range of variation necessary to illustrate in a connected manner all typical cases.

Referring to Fig. 4, the lines joining E and M represent the to-and-fro signals of light which are separated to show the passage each way. E signals to M that it is 12 o'clock at the moment the flash is sent off. M receives the signal at 12:1, and signals back to E that the return flash was instantly sent back at 12:1. E gets it at 12:2. The time taken in sending and receiving signals is therefore a minutes. The watches are set so that when it is 12 o'clock on E it is 12 o'clock on M: the signals confirm this. The watches are together from an imaginary observer's point of view so stationed that he can look at both watches simultaneously, i.e., the observer may be regarded as moving with the system. The "time" is not different from the usual conception of the simultaneousness of events. If E and M were stationary the results would be exactly the same. It is important to note here that the light-source remains in the centre of the waves it origin-

* We may assume a distance that would give this value, and of course our choice of "12 o'clock" is quite arbitrary.

ates, and this observation applies in the following cases when we take into account the new definition of time and the consequences of the principle involved.

The change in the *unit of time* renders the light velocity measured perpendicular to the line of motion in a given system (Fig. 4) the same as if the system were stationary. The ratio being—

$$\frac{1}{\sqrt{1 - \frac{v^2}{c^2}}}$$

c =velocity of light. v =velocity of the system. This means in effect that in Fig. 4 E and M do not drift away from the light-disturbance, the latter becoming to all

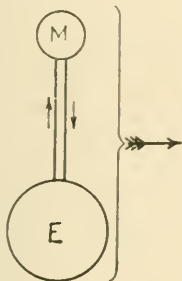


FIG. 4.

intents and purposes a fixture joining E and M. Similarly, the change in the *unit of length* in the direction of motion is reduced in the ratio—

$$\sqrt{1 - \frac{v^2}{c^2}}$$

and these fundamental changes have to be taken into account.

The equation for the *difference in time* between two watches separated by a distance l and moving in a direc-

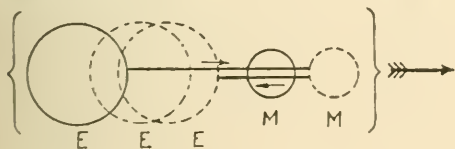


FIG. 5.

tion coincident with the line joining them is of interest in this connection. This is—

$$\frac{v l}{c^2 \sqrt{1 - \frac{v^2}{c^2}}}$$

Referring to Fig. 5, E and M are moving together through space in the manner shown (the third position of M is not outlined as it does not come into consideration). E signals to M that it is 12 o'clock, as before; M gets the signal at 12:1½ owing to movement, and immediately sends back word that the signal arrived at 12:1½. E in the meantime has also moved in space relatively to the light disturbance that was sent off from M, and in consequence meets the return signal at 12:2½. Now 12:2½—12:1½ does not equal 12:1½—12:0. Therefore E concludes that M's watch is fast (*i.e.*, ahead in time), and E consequently tells M to set back her watch to 12:1½ at the next noon-signalling, so that 12:2½—12:1½ equals 12:1½—12:0, as by this principle the times of transit each way must be equal. Referring back to Fig. 4, the

to-and-fro light-distance was 2 minutes, whereas it is now 2½ minutes. This means that we must, from the point of view of the system, consider it contracted in the direction of motion sufficient to reduce the excess time to zero, so that by the principle of equal transits 12:2—12:1=12:1—12:0, as in Fig. 4; this applying when the movement changes to that of Fig. 5. From a stationary outside observer's point of view, which is a "relativity" view, the second is lengthened, and the unit of length appears in consequence shorter to the stationary observer, and the forward watch is behind in time. Thus it will be seen that when the two watches are together in time by signalling they are to an outside observer not together as before: M's watch is behind in time. If the direction of motion were reversed, M's watch would have to be advanced which would make the results the same as in this case. Einstein says:—"Two events which are simultaneous when regarded from one co-ordinate system, are not to be regarded as simultaneous when considered from a co-ordinate system which is in motion with respect to the first."

This change in time (about 22 seconds in our example) has been occasioned by the translational movement in the direction indicated by the arrow, and these times (in the relativity sense simultaneous events) are the true relatively physical times when the system is considered in movement as shown.*

Referring now to Fig. 6, E is "stationary" in space, but M (at M₁) sets off moving steadily away, so that at successive intervals her position is M₂, M₃, &c. We have for convenience assumed a very high velocity of M: just short of that of the light. E signals to M that it is 12 o'clock, as before; M gets the message at 12:2 as she has moved along (we may assume that the message was sent off from E at such a time as to give this result, or rather, that the movement of M was started at such a time just before the arrival of the signal at M₁—as to enable the light disturbance to overtake her at 12:2). M instantly sends back word that it arrived at 12:2, and E gets this return signal at 12:4. E, therefore, finding a change in M's time immediately signals this circumstance, but M does not get the message in the expected time, noting a still further delay, and she concludes that her watch is running fast. M therefore regulates her watch so that in the reciprocation of signals her time is in proper agreement with that of E. M's watch is then running slow and consequently losing time relative to that of E, but this change in her *unit of time*, say the "second," has been brought about by the *relative movement*.

This looks like juggling with time. It is juggling with practically *all* physical phenomena, for, besides time, *space* and *length* become involved as we have already seen. Whether we are justified in turning topsy turvy our old established ideas of these fundamental concepts is not to be discussed here, the object being to present the ideas clearly and fairly. There is undoubtedly a deeper meaning behind the principles than would appear on the surface;† and it is hardly a correct statement to say that time is thereby rendered *discontinuous*, any more than it is fully correct to say—Because an alternating current can be resolved into current-components the corresponding E.M.F. components, which must follow, are themselves isolated or discontinuous phenomena.

* In regard to the synchronising of the watches, this may be expressed in the following way:—"Let an observer stationed at *a* send a flash of light at the instant *t_a* (as indicated by the *a*-clock) towards *b*, where it arrives at the instant *t_b* (according to the *b*-clock). Let another observer send it back from *b* without any delay, or let the flash be automatically reflected at *b*, towards *a*, where it returns at the instant *t'_a*. Then the *b*-clock is said, by definition, to be *SYNCHRONOUS* with the *a*-clock, if

$$t'_a = t_b = t_a - t_a'' \text{—SILBERSTEIN.}$$

† For instance, we must bear in mind that the term or expression *velocity of light* has a deep-seated significance, in that it is an outward expression of an inward mechanism of matter, and we should not think of it superficially as a mere velocity.

We must remember that, in the relativity sense, time is as much a phenomenon as anything else. This is interesting from another point of view. We cannot conceive the beginning of things or the end of space, therefore we are perhaps justified in considering the relativity idea of space and time as phenomena of experience in distinction from a thing that can be rounded up in our imaginations, or, as Mr. Redgrove has put it, there is nothing more in a phenomenon than its appearance: from, of course, this point of view I may add (see concluding part).

If the principles involved have a wide application or expression in the cosmical sense, they must obtain in the immediate world round us, *e.g.*, in the laboratory. It was evidently necessary to make use of highly artificial concepts to establish fundamentally on a broad basis the ideas involved. The velocity of light in space (or a vacuum) is about 300,000,000 metres per second, hence long-distance phenomenon, so to speak, is chosen to show appreciable differences. The theory cannot be made comprehensible entirely by the methods employed, but, by its application it can help to explain and co-ordinate certain physical phenomena. It may be useful, just as mathematical devices are useful, in fact it is an extended mathematical device, or we may so regard it from one viewpoint.

Returning now to the contraction idea, we can begin to get an inkling of how this conception may be supplanted by the wider one under consideration. We may for convenience conceive the Michelson-Morley experiment

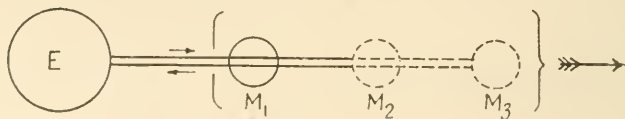


FIG. 6.

conducted in a vacuum, since the presence of air does not enter properly into consideration. Here we have a fixed light-velocity, though the apparatus is moving, but the principle of relativity involves alterations in the "fundamentals" in the same relative proportion, so that the physical laws preserve their identity unchanged to us who are observers moving with the entire apparatus, including (which is the important thing) the light source. We cannot therefore detect this change; consequently, there is a cancelling out so to speak, so that nothing happens—no difference-phenomenon is observable. This brings us formally to the first postulate of the theory, which Prof. Wood renders as follows:—

"The theory of relativity starts out with two postulates. The first of these states that uniform motion of translation cannot be measured or even detected by an observer stationed on the moving system from observations confined to the system. This amounts to saying that motion through the æther (if the æther exists at all) will be wholly without influence upon all optical experiments made with terrestrial sources of light." The second postulate was stated above. (The heavy-faced type is mine).

Campbell, in his "Modern Electrical Theory," 1913 (Cambridge University Press), says that the most complete account of the relativity principle or principles here discussed is given by Einstein himself in *Jahrbuch d. Radioaktivität u. Elektronik*, 1907, iv., 411. Campbell speaks highly of a paper by Bumstead in *Am. Journ. of Science*, 1908, xxvii., 493. I will quote a few lines:—Einstein's "fundamental postulate amounts to a denial that it is possible to observe any effects of uniform convection through the æther in which all the bodies concerned (including the observer) take part. This he calls the Principle of Relativity; the significance of the name is that only relative motion of one portion of matter with respect to another, or one electrical charge with respect to another, can produce any observable effect; uniform motion, relative to

the æther alone, becomes as impotent, if not meaningless, as absolute motion." See also Richardson's "Electron Theory of Matter," recently published by the Cambridge University Press.

(To be continued).

THE DETERMINATION OF NITRIC NITROGEN IN SOILS.*

By E. R. ALLEN.

Object of the Research.

THE determination of nitric nitrogen has been the subject of a very large amount of experimentation, discussion, and controversy. In spite of the array of methods that have been proposed, more or less uncertainty exists in the use of any one of them, as is shown, for instance, by the following statements:—"No single method appears to be applicable to the determination of nitrogen in nitrates in all classes of water, sewages, and sewage effluents, and there is no method which is not subject to considerable error" ("Standard Methods of Water Analysis," American Public Health Association, 1912, 23); and, "The accurate determination of nitric acid in combination presents great difficulties and can be made only by indirect means;" the methods here given are sufficient for most purposes. Very few of them can be said to be simple, but it is to be feared

that no simple process can ever be obtained for the determination of nitric acid in many of its combinations" (Sutton, "Volumetric Analysis," 1910, 10th ed., 271).

In our investigations on the physiology of the process of nitrification in soils we have been confronted at the outset with the uncertainty of the methods and the paucity of information regarding the probable errors of the same. In reading the literature quite extensively, we have been impressed by the non-uniformity of methods employed by physiologists, and in many cases it is impossible to decide how many of the differences reported are due to differences in physiology and how many to analytical errors.

Another source of error contributing to the confusion of the existing data on the nitric nitrogen problem is that it is not certain that the prevailing methods of extracting the soil actually recover all the nitric nitrogen. The object of the present research will be, however, to develop a method suitable for the study of the physiology of nitrification. A second paper will be devoted to the separation of ammonia, nitric and organic nitrogen, and a third to the extraction of nitric nitrogen from soils.

Requirements to be Met.—A method to meet the requirements of the physiological study of nitrification should be applicable to amounts of nitrate nitrogen varying from 0.1 to 25.0 mgrms. contained in each case in 250 cc. of soil extract, therefore in the presence of organic matter. The error should be of the order of magnitude of 2 per cent or less. 100 grm. portions of soils are convenient amounts with which to work in nitrification studies. If this amount is extracted with five times its weight of water, for instance, and an aliquot (usually 250 cc.) taken for analysis, then with samples containing 2, 100, and 500 parts nitric nitrogen per million of soil, and intermediate values, as may be met in nitrification studies, an error of 2 per cent would require an analytical procedure, the

* From the *Journal of Industrial and Engineering Chemistry*, vii., No. 6.

probable error of which would be ± 0.002 , ± 0.10 , and ± 0.5 of a mgrm. for the amounts named. The method should also permit the determination of ammonia nitrogen in the same sample.

Historical: Reduction Methods.

A review of all the literature on methods of nitric nitrogen determination would be scarcely possible or desirable. It is obvious that reduction methods, provided they proceed rapidly and quantitatively, are the most desirable, since nitrogen is more easily and more accurately measured as ammonia than in any other form; small amounts may be accurately determined colorimetrically, while larger amounts may be very satisfactorily determined by titration. However, the fact that reduction methods have by no means been adopted to the exclusion of other procedures indicates that they do not give uniformly reliable results; indeed many instances are recorded in the literature in which chemists have failed to agree on reduction procedures. The careful and thorough work of Mitscherlich and Herz (*Landw. Jahrb.*, 1909, xxxviii., 279) clears up much in this connection; they conclude that most reduction methods are burdened with errors; that, however, reduction with Devarda's alloy does give quantitative results, and that by proper refinement of the distillation apparatus and of the titrimetric procedures a very high degree of accuracy may be attained.

The Devarda Method (*Zeit. Anal. Chem.*, 1894, xxxiii., 113; Treadwell-Hall, "Analytical Chemistry," 1913, 3rd ed., ii., 454) consists of reducing nitric nitrogen in strongly alkaline solution with a finely divided alloy composed of 50 per cent copper, 45 per cent aluminum, and 5 per cent zinc. It is the only method, so far as we are aware, that has escaped serious criticism in the literature. While its superiority over other methods has been questioned by some, we have not found a case in which the reliability of the method itself has been questioned. According to W. S. Allen (original communication, Eighth International Congress Applied Chemistry, New York, 1913, i., 19) it gives reliable results, and Cahen (*Analyst*, 1910, xxxv., 307) regards it as satisfactory and vastly superior to Pozzi-Escot's method (reduction with aluminum-mercury couple). After trying different reduction methods Valmari ("Unter. ü. d. Lösbarkeit u. Zersetzbarkeit d. Stickstoff im Boden," 1912, Dissertation, Helsingfors, 43) concluded that a finely powdered copper-aluminum alloy, to which a small amount of zinc had been added to produce brittleness—to which class, therefore, Devarda's alloy belongs—is the best reducing agent for nitric nitrogen. Mitscherlich and Herz (*loc. cit.*) conducted an extended investigation on the perfection of an accurate Kjeldahl method which would include all forms of nitrogen, in course of which they studied, among other sources of error, the question of the reduction of nitric nitrogen. Using phenolsulphonic acid and zinc dust, sodium hydroxide and zinc-iron dust, Jodlbauer's method and Förster's method, they were unable to obtain the theoretical amount of ammonia from nitrate. Because they were unable to recover the deficiency of nitrogen by digesting the residues according to Kjeldahl for total nitrogen, and because the use of larger amounts of reducing materials did not lessen the losses, they concluded that the "nitrogen loss is not to be attributed to an unfinished, and therefore incomplete reduction, but is much more likely due to the fact that gaseous nitrogen is evolved during the procedure. This loss can be avoided only through other reduction media. As such a one we have chosen Devarda's alloy (*loc. cit.*, 317).

Besides pointing out that the Devarda procedure is the best for effecting reduction of nitric nitrogen, Mitscherlich and Herz also Valmari proposed modifications of the original procedure.

The Mitscherlich-Devarda Method differs from the original Devarda method in the apparatus used, which

effectively prevents the carrying over of alkaline spray into the receiver and still retains the advantage of ease of transfer of the ammonia from distilling-flask into receiver, while avoiding the error due to the solubility of the alkali of a glass distillation tube and to the slight absorbing action on ammonia of block-tin condenser tubes. Using this apparatus Mitscherlich and Herz obtained excellent results. From ten determinations, on each of four known amounts of nitrogen, they obtained these results (*loc. cit.*, 289):—

Cubic Centimetres, N/50 H₂SO₄.

No.	Average.	Probable error.	True value.
I. ..	24.335	± 0.070	24.40
II. ..	12.15	± 0.044	12.20
III. ..	6.095	± 0.025	6.10
IV. ..	2.44	± 0.021	2.44

Mgrms. Nitrogen.

No.	True value.	Probable error.	Deviation from true value.
I. ..	6.84	± 0.02	-0.018
II. ..	3.42	± 0.012	-0.014
III. ..	1.71	± 0.007	-0.001
IV. ..	0.68	± 0.006	-0.000

They conclude:—"These results show better than any words that in our hands the reduction of the nitrate nitrogen is complete, and that the error of this analysis has not become greater than that of the ammonia distillation." The source of the nitrate nitrogen in these analyses was potassium nitrate, which gave the theoretical amount of potassium sulphate. Mitscherlich and Herz conclude their paper by saying:—"From the preceding work it is worthy of note that hitherto performed nitrate nitrogen analyses are burdened with very great errors, because great losses occur in the reduction processes" (*loc. cit.*, 318).

The Valmari-Devarda Method possesses the distinctive feature that reduction is carried out in dilute alkaline solution, whereas strong alkali is required by the original directions of Devarda. According to Valmari, the reaction of a copper-aluminum-zinc alloy is electrolytic, innumerable small cells being formed with aluminum as anode and copper as cathode. The potential difference is, however, not enough to decompose water at room temperature. Boiling produces an evolution of hydrogen, and this evolution is much increased if the conductivity of the water is increased by the presence of neutral electrolytes, and a very low concentration of alkali—even that imparted to the solution by magnesium oxide—hastens the actions sufficiently to reduce nitrate rapidly and quantitatively to ammonia. The nitrogen of a nitrate solution may be distilled off with magnesium oxide and a finely divided copper-aluminum-zinc alloy in a 30-minute distillation period, just as if it were a solution of an ammonium salt.

Valmari found that in solutions high in organic matter the reaction is retarded so that the evolution of hydrogen is not sufficient to effect quantitative reduction. Satisfactory results are obtained by the addition of 5 cc. of the sodium hydroxide solution used in Kjeldahl determinations, which makes the solution about N/10 in NaOH. Valmari also recommends the altering of the composition of Devarda's alloy, pointing out that the percentage of aluminum should be higher, but that the brittleness of the mixture sets a certain limit that must not be overstepped. The proportions of 60 per cent aluminum, 37 per cent copper, and 3 per cent zinc give an alloy still capable of being pulverised.

The Aluminum Reduction Method, which has been used with varying success in water analysis, has recently been recommended by Burgess for the determination of nitrates in soil extracts (University of California Publications in Agr. Sci., 1913, i., No. 4). The procedure used is described later. The fact that the somewhat extravagant conclusions are drawn that "the aluminum reduction

method for the determination of nitrates in soils yields the most accurate results of all methods now commonly in vogue," and that "the presence of extraordinarily large amounts of soluble organic materials (soluble humus and dextrose) have little effect on the method," and also the fact that the Associate Referee of the Association of Official Agricultural Chemists on nitrogenous materials in soils (*American Fertiliser*, 1914, xli., 33) recommends the adoption of this as an official method, caused us to include some tests of it in this work.

Discussion.—Although the power of Devarda's alloy to reduce nitric nitrogen to ammonia quickly and quantitatively is apparently agreed upon, the original Devarda method possesses two sources of error:—1. Owing to the rapid evolution of hydrogen some fine alkaline spray is likely to be carried over into the receiver, necessitating the redistillation of the receiver contents over MgO. 2. In solutions high in organic matter, as are frequently encountered in soil extracts, the action of the strong alkali on the organic matter is so marked that a sharp separation of the nitric from the organic nitrogen is not possible. The Mitscherlich-Devarda method eliminates the first of these errors and retains the second (see Note 1), while the Valmari-Devarda procedure reduces both, but, except in the case of reduction in MgO solutions, when there is no danger of spray going over, completely eliminates neither. The aluminum reduction method also used a much more dilute alkaline solution for reduction than that employed in the Mitscherlich-Devarda method. However, neither Valmari nor Burgess gave the extended attention to the refinement of the methods they recommended that Mitscherlich and Herz gave to theirs. Before, therefore, these methods, employing more dilute alkaline solutions, could be accepted they had to be as rigidly examined as the Mitscherlich-Devarda method had been. If a method applicable in the presence of organic matter, in which the reduction is carried out in weakly alkaline solutions, could be developed to a point where its probable error was of the order of magnitude obtained by Mitscherlich and Herz, it would surpass any that has yet appeared, and we could hope to later perfect the separation of the nitric from the organic nitrogen, and thus attain our original object. The comparison of the reduction procedures used in the aluminum reduction, Mitscherlich-Devarda, and Valmari-Devarda methods, the determination of conditions affecting quantitative reduction, and the determination of the probable error of the method furnishes the basis of the experimental part of this work.

(To be continued).

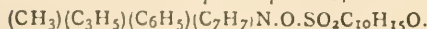
STUDIES IN THE STEREOCHEMISTRY OF QUINQUEVALENT NITROGEN.*

RESOLUTION OF THE ASYMMETRIC QUATERNARY AMMONIUM COMPOUNDS.

By SHIGERU KOMATSU.

(Continued from p. 239).

C. α -Dextro Methyl Allyl Phenyl Benzyl Ammonium Dextro-camphorsulphonate,



In June the author attempted the resolution of α -methyl allyl phenyl benzyl ammonium iodide by means of dextro-camphorsulphonate (Pope and Harvey, *Journ. Chem. Soc.*, 1899, lxxv., 1127), and on standing the acetone solution of the reaction product in a desiccator, kept in a dark and cold place for a week, the crystals began to separate out from the solution, but its yield was very poor. The substance re-crystallised five times from acetone consisted of colourless needles which were found to melt at 161° to

162° . They are soluble in water, acetone, ethyl acetate and alcohol; their analysis gave the following result:—
0.178 grm. substance gave 0.0878 grm. BaSO_4 .

Sulphur calculated for $\text{C}_{27}\text{H}_{38}\text{O}_2\text{NS}$.. 6.82
Sulphur found 6.78

The rotatory power of the substance was determined in an aqueous solution, with the following results:—

(a). A solution of 0.8525 grm. substance made up to 25 cc. with water at 25° , gave $\alpha_D 25 = +3.17^\circ$ in a 20 cm. tube; whence $[\alpha]_D 25 = +46.48^\circ$.

(b). A solution of 0.5327 grm. substance made up to 25 cc. with water at 25° , gave $\alpha_D 25 = +2.02^\circ$ in a 20 cm. tube; whence $[\alpha]_D 25 = +47.40^\circ$.

Adding potassium iodide to the mother-liquor separated from dextro methyl allyl phenyl benzyl ammonium d-camphorsulphonate, laevo methyl allyl phenyl benzyl ammonium iodide was obtained in an impure state; the substance re-crystallised from ethyl alcohol was found to melt at 127° to 128° , and the specific rotatory power to be $[\alpha]_D 25 = -29.33^\circ$ in alcoholic solution.

In the second experiment performed in winter, the yield of racemic methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate was more fruitful than in the previous experiment; it was macerated with ethyl acetate according to Pope and Harvey (*loc. cit.*).

The first crop consisted of colourless needles; after evaporating the mother-liquor to a small bulk, and then on standing it over sulphuric acid, we get the second crop.

From the mother-liquor of the second crop, rhombic crystals deposited as the third crop. Evaporating the residual liquor almost to dryness, and then adding a large quantity of ether, hygroscopic crystals were formed, and finally the syrupy residue was dissolved in water and converted into the iodide.

For each fraction the optical measurement was made in its aqueous solution, and the results will be mentioned below.

The First Fraction.—The crystals obtained by re-crystallising from ethyl acetate five times melted at 162° , and the optical rotation for each of four pure preparations a, b, c, and d was determined.

(a). A solution of 0.2082 grm. substance made up to 25 cc. with water at 25° , gave $\alpha_D 25 = +0.77^\circ$ in a 20 cm. tube; whence $[\alpha]_D 25 = +46.23^\circ$.

(b). A solution of 0.1423 grm. substance obtained by the re-crystallisation twice from acetone, made up to 25 cc. with water at 25° , gave $\alpha_D 25 = +0.54^\circ$ in a 20 cm. tube; whence $[\alpha]_D 25 = +47.43^\circ$.

(c). A solution of 0.3132 grm. substance made up to 25 cc. with water at 25° , gave $\alpha_D 25 = +1.17^\circ$ in a 20 cm. tube; whence $[\alpha]_D 25 = +46.67^\circ$.

(d). A solution of 0.3176 grm. substance made up to 25 cc. with water at 25° , gave $\alpha_D 26 = +1.20^\circ$ in a 20 cm. tube; whence $[\alpha]_D 25 = +47.23^\circ$.

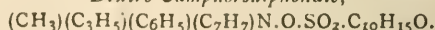
The mean value is therefore $[\alpha]_D 26 = +46.91^\circ$, while Jones (*loc. cit.*) on one hand and Pope and Harvey (*loc. cit.*) on the other gave $[\alpha]_D = +46.8^\circ$ and $[\alpha]_D = +46.6^\circ$ respectively.

The Second Fraction.—A solution of 0.3168 grm. substance made up to 25 cc. with water at 25° , gave $\alpha_D 25 = +0.97^\circ$ in a 20 cm. tube; whence $[\alpha]_D 25 = +38.27^\circ$.

The Third Fraction.—A solution of 0.1983 grm. substance made up to 25 cc. with water at 25° , gave $\alpha_D 25 = 0$ in a 20 cm. tube.

The Fourth Fraction.—A solution of 0.2382 grm. substance made up to 25 cc. with water at 25° , gave $[\alpha]_D 25 = -0.07^\circ$ in a 20 cm. tube; whence $[\alpha]_D 25 = -1.32^\circ$.

D. γ -Dextro Methyl Allyl Phenyl Benzyl Ammonium Dextro Camphorsulphonate,



A. Equimolecular mixture of γ -methyl allyl phenyl benzyl ammonium iodide and silver dextro camphorsulphonate was heated in an acetone-ethyl acetate solution for two and a-half hours on a water-bath. From the reaction

* *Memoirs of the College of Science, Kyoto Imperial University*, 915, i, No. 9.

product, dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate was obtained in the like manner as was described in the case of the *a* compound, the substance crystallising from acetone in white needles, and melting at 162°.

It is soluble in alcohol, acetone, ethyl acetate, and water, but not in ether. The sulphur contents and the rotatory power of the substance were determined with the following results:—

0.2101 grm. of the substance gave 0.1043 grm. BaSO₄.

Sulphur calculated for C₂₇H₃₅O₄NS .. 6.82

Sulphur found 6.82

(a). A solution of 1.8444 grm. substance made up to 25 cc. with water at 25°, gave α_D 25 = +3.87° in a 20 cm. tube; whence [α]_D 25 = +57.29°.

(b). A solution of 0.9161 grm. of the substance made up to 25 cc. with water at 25°, gave α_D 25 = +4.37° in a 20 cm. tube; whence [α]_D 25 = +59.63°. The mean value of the rotatory power is therefore accounted for as [α]_D 25 = +58.46°.

The filtrate from the crystals of dextro ammonium dextro-camphorsulphonate was dissolved in water, and then potassium iodide solution added to transform the base contained in it into the iodide whose rotatory power in an alcoholic solution has been observed to be [α]_D 25 = -25.0°.

B. As the second experiment, the racemic dextro-camphorsulphonate was subjected to the fractional crystallisation in ethyl acetate, and the pure γ-dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate obtained consisted of white needles which melt at 163° to 164°. The determination of the rotatory power of the substance was conducted with the purified different preparations *a*, *b*, and *c* in their aqueous solutions.

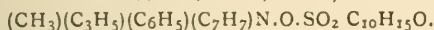
(a). A solution of 0.2532 grm. substance made up to 25 cc. with water at 25°, gave α_D 25 = +1.20° in a 20 cm. tube; whence [α]_D 25 = +59.24°.

(b). A solution of 0.2342 grm. substance obtained by the re-crystallisation of the preparation (a) from acetone, made up to 25 cc. with water at 25°, gave α_D 25 = +1.10° in a 20 cm. tube; whence [α]_D 25 = +58.71°.

(c). A solution of 0.3572 grm. of the same preparation as used in (b) made up to 25 cc. with water at 25°, gave [α]_D 25 = +1.67° in a 20 cm. tube; whence [α]_D 25 = +58.44°.

The mean value of the specific rotatory power is therefore accounted for as [α]_D 25 = +58.66°.

E. α-Lævo Methyl Allyl Phenyl Benzyl Ammonium Lævo camphorsulphonate,



A. By the interaction of 5 grms. raw α-lævo methyl allyl phenyl benzyl ammonium iodide and 5 grms. silver lævo-camphorsulphonate, 2.5 grms. lævo methyl allyl phenyl benzyl ammonium lævo-camphorsulphonate was obtained in pure state.

The substance re-crystallised from acetone three times, melts at 160° to 161°, and has the same chemical and physical properties as its enantiomorphous salt. The specific rotatory power in its aqueous solution was determined to be opposite in its sign to that of its antipode, but with the same magnitude as will be shown in the following statements:—

(a). A solution of 0.3069 grm. substance made up to 25 cc. with water at 25° gave α_D 25 = -1.14° in a 20 cm. tube; whence [α]_D 25 = -46.43°.

(b). A solution of 0.2927 grm. substance made up to 25 cc. with water at 25°, gave α_D 25 = -1.09° in a 20 cm. tube; whence [α]_D 25 = -46.55°.

The analytical result is as follows:—

0.3097 grm. of the substance gave 0.1533 grm. BaSO₄.

Sulphur calculated for C₂₇H₃₅O₄NS .. 6.82

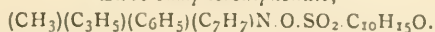
Sulphur found 6.80

B. The substance also prepared from 6 grms. α-methyl allyl phenyl benzyl ammonium iodide and 6 grms. silver lævo camphorsulphonate in an acetone-ethyl acetate solution, and its yield in pure state was found to be about 1 grm.

The pure preparation melting at 162° to 163° gave the following value of the optical rotatory power in an aqueous solution.

A solution of 0.2249 grm. substance made up to 25 cc. with water at 25°, gave α_D 25 = -0.84° in a 20 cm. tube; whence [α]_D 25 = -46.69°.

F. γ-Lævo Methyl Allyl Phenyl Benzyl Ammonium Lævo-camphorsulphonate,



A. Four grms. crude γ-l-methyl allyl phenyl benzyl ammonium iodide (its specific rotatory power in alcohol solution being [α]_D 25 = -25.0°) was made to react with 4 grms. silver l-camphorsulphonate in an acetone-ethyl acetate solution, and 1 grm. pure γ-l-methyl allyl phenyl benzyl ammonium l-camphorsulphonate was obtained. It crystallises from acetone in white needle-shaped crystals which melt at 163° to 164°, possessing all the other same chemical and physical properties as those of its antipode.

0.357 grm. of the substance gave 0.1792 grm. BaSO₄ by analysis.

Sulphur calculated for C₂₇H₃₅O₄NS .. 6.82

Sulphur found 6.89

A solution of 0.2581 grm. substance made up to 25 cc. with water at 25°, gave α_D 25 = -1.09° in a 20 cm. tube; whence [α]_D 25 = -55.70°.

A solution of 0.2422 grm. substance made up to 25 cc. with water at 25°, gave α_D 25 = -1.09° in a 20 cm. tube; whence [α]_D 25 = -56.21°.

B. Pure γ-lævo methyl allyl phenyl benzyl ammonium lævo-camphorsulphonate was also prepared by the interaction of 6.5 grms. γ-racemic methyl allyl phenyl benzyl ammonium iodide and 6 grms. silver lævo-camphorsulphonate, and its yield was found to be about 1.5 grms.

The melting-point of the substance was observed to be 162° to 163°, and its specific rotatory power was determined in an aqueous solution.

A solution of 0.2244 grm. substance made up to 25 cc. with water at 25°, gave α_D 25 = -1.02° in a 20 cm. tube; whence [α]_D 25 = -56.82°.

(To be continued).

RADIOMETRIC MEASUREMENTS OF THE IONISATION CONSTANTS OF INDICATORS.*

By E. J. SCHAEFFER, M. G. PAULUS, and HARRY C. JONES.

(Continued from p. 242).

Phenolphthalein.—Regarding phenolphthalein as a monobasic acid, we have from Equation 2:—

$$\frac{\bar{Q} \times \bar{H}}{LH} = K_i.$$

Dividing this by the ion product of water, it follows that:—

$$\frac{LH \times \bar{OH}}{Q^+} = \frac{K_w}{K_i} \dots \dots (21).$$

Phenolphthalein has but one component of absorption, and the application of Beer's law is much simpler than for methyl-orange where there are two components of absorption. A solution of phenolphthalein in pure water is perfectly transparent. The addition of an excess of sodium hydroxide converts all the colourless lactoid molecules into

* From the *Journal of the American Chemical Society*, xxxvii., No. 4.

the red quinoid salt, the concentration of which we will represent by c' . Let c be the concentration of the quinoid salt in the phenolphthalein solutions containing ammonium hydroxide and ammonium chloride. Since the depth of solution was maintained constant, we have the two fundamental equations given below:—

$$\ln(I/I_0) = -Kc \quad \dots \quad (22).$$

$$\ln(I/I_0)' = -Kc' \quad \dots \quad (23).$$

The constant K is the same in both cases. Dividing 22 by 23 we obtain:—

$$\frac{\ln(I/I_0)}{\ln(I/I_0)'} = c'/c \text{ or } c = \frac{c' \times \ln(I/I_0)}{\ln(I/I_0)'} \quad \dots \quad (24).$$

Where $(I/I_0)'$ is the percentage transmission of a solution of phenolphthalein containing an excess of alkali, for some given wave-length of light; (I/I_0) that for the solution in which the concentration of the quinoid salt c , is to be determined for the same wave-length of light. Knowing then the amount of phenolphthalein converted into the quinoid salt, LH in Equation 21 is given by $T-c$, where T represents the total amount of phenolphthalein. The hydroxyl ion concentration was varied by the addition of ammonium chloride to ammonium hydroxide.

The value of OH to be substituted in the hydrolysis equation for phenolphthalein was obtained from the following equation:—

$$\frac{NH_4 \times OH}{(NH_4OH + NH_3)} = K_b.$$

If ammonium chloride and ammonium hydroxide are present in the same solution, the concentration of the NH_4 ions is furnished almost entirely by the ammonium chloride. Let S equal the concentration of the salt and B the concentration of the base. We then have for dilute solutions:—

$$\frac{S \times OH}{B} = K_b \quad \dots \quad (25),$$

or—

$$OH = \frac{K_b \times B}{S} \quad \dots \quad (26).$$

The ionisation constant for ammonium hydroxide (Carnegie Institution of Washington, 1907, *Publication* No. 63, p. 298) at 25° is given as 18×10^{-6} . All of the work on phenolphthalein was done at 20° , and reducing the above value to 20° we obtain from Equation 26, q being equal to 1400 calories, $K_b = 17.4 \times 10^{-5}$.

TABLE X.

(I/I_0 for depth of solution = 20 mm.).

$\lambda = A.U.$	I.	II.	III.	IV.	V.
5773	10.5	10.1	12.1	10.1	24.9
5798	15.2	15.4	16.5	15.2	31.0
5823	20.8	20.2	22.6	21.4	37.8
5848	28.7	27.4	30.3	28.4	45.6
5947	59.4	57.7	61.2	60.3	71.1

A pure sample of phenolphthalein was re-crystallised from absolute methyl alcohol. A weighed amount of purified phenolphthalein was dissolved in 50 cc. of absolute ethyl alcohol. By means of a small pipette, carefully calibrated, a small volume of this alcoholic solution, say, 1.25 cc., could be quite accurately measured. This volume was diluted with conductivity water to 2000 cc. Experiments were made which showed that the effect of this small trace of alcohol was negligible. (See McCoy, *loc. cit.*). The ammonia employed for the solution of ammonium hydroxide was distilled from barium hydroxide to eliminate carbon dioxide. All solutions were prepared with conductivity water at 20° . Special care was taken to prevent carbon dioxide from coming in contact with any of the solutions.

TABLE XI.

(I/I_0 for depth of solution = 20 mm. Temperature = 20°).

Solution I.	75 cc. phenolphthalein diluted to 100 cc.
II.	75 cc. phenolphthalein, 2 cc. NH_4OH , 1 cc. NH_4Cl , diluted to 100 cc.
III.	75 cc. phenolphthalein, 2 cc. NH_4OH , 2 cc. NH_4Cl , diluted to 100 cc.
IV.	75 cc. phenolphthalein, 2 cc. NH_4OH , 5 cc. NH_4Cl , diluted to 100 cc.
V.	75 cc. phenolphthalein, 2 cc. NH_4OH , 10 cc. NH_4Cl , diluted to 100 cc.
VI.	75 cc. phenolphthalein, 1 cc. $N NaOH$, diluted to 100 cc.

$\lambda = A.U.$	I.	II.	III.	IV.	V.	VI.
5773	100.0	30.8	46.3	70.7	—	10.1
5798	100.0	37.8	53.4	76.3	86.7	14.3
5823	100.0	45.3	58.9	78.5	89.3	20.2
5848	100.0	51.7	66.2	83.0	91.3	27.4
5948	100.0	—	83.7	—	—	57.7

TABLE XII.

Solu- tion.	$\lambda =$ A.U.	Lactoid form. $c \times 10^5$.	Quinoid salt. $c \times 10^5$.	$OH \times 10^5$.	K_w/K_i $\times 10^5$.	$K_i \times 10^{10}$.
II.	5773	2.44	2.58	5.039	4.77	1.70
	5798	2.51	2.51	5.039	5.05	1.60
	5823	2.54	2.48	5.039	5.17	1.57
	5848	2.46	2.56	5.039	4.85	1.67

Average 1.63

III.	5773	3.33	1.69	2.519	4.96	1.64
	5798	3.40	1.62	2.519	5.27	1.54
	5823	3.35	1.67	2.519	5.06	1.60
	5848	3.42	1.60	2.519	5.38	1.51
	5948	3.40	1.62	2.510	5.28	1.53

Average 1.56

IV.	5773	4.26	0.757	1.007	5.68	1.43
	5798	4.32	0.696	1.007	6.27	1.29
	5823	4.26	0.761	1.007	5.63	1.44
	5848	4.30	0.720	1.007	6.02	1.35

Average 1.38

V.	5798	4.65	0.369	0.503	6.37	1.27
	5823	4.67	0.356	0.503	6.63	1.22
	5848	4.67	0.352	0.503	6.68	1.21

Average 1.23

It is well known that an excess of alkali causes a rather rapid fading of solutions of phenolphthalein. Experiments were made which showed that a very slight error would be introduced if the solutions of phenolphthalein containing an excess of alkali were used directly after being prepared. Filling the cells with the solution, and taking radiometric measurements for five wave-lengths of light, required about eight minutes, and during this short space of time the change in transparency was found to be very slight.

A few of the experiments made with solutions of phenolphthalein containing an excess of alkali are recorded in Table X. All solutions were diluted to 100 cc., and each contained equal amounts of phenolphthalein. A normal solution of sodium hydroxide was used for these experiments. The percentage transmissions given by Solutions I. and II. are for 0.8 cc. and 1 cc. respectively of the alkali. The interval which elapsed between the time the solutions were prepared and the last measurement made was between seven and eight minutes. Measurements were again made with Solution II. fifteen minutes later. The results are recorded under III. By comparing the transmission values, the effect of the bleaching for an interval of fifteen minutes can be noted. Solution IV.

contained 0.5 cc. alkali, and was kept in the dark nearly a half-hour before being used. Solution V., containing 1 cc. of alkali, was used about four hours after being prepared.

Similar experiments were made with solutions of phenolphthalein, partially converted into the quinoid salt, and it was found that such solutions are fairly stable. Very little change in transparency could be detected during the first four or five hours after the solutions were prepared.

Results with Phenolphthalein.—The six solutions recorded (Table XI.) were prepared from the following mother solutions:—The concentration of the phenolphthalein was 6.697×10^{-5} grm.-molecules per litre, that of the ammonium hydroxide 0.1448 grm.-molecule per litre, and that of the ammonium chloride 0.1 grm.-molecule per litre.

The percentage transmissions for these solutions are given in Table XI. The concentrations of the two tautomeric forms, and the hydrolysis and ionisation constants calculated from Table XI., are recorded in Table XII.

TABLE XIII.

(I/I₀ for depth of solution = 20 mm. Temperature = 20°).

Solution I.	75 cc. phenolphthalein, 1 cc. NH ₄ OH, 0.5 cc. NH ₄ Cl, diluted to 100 cc.
" II.	75 cc. phenolphthalein, 1 cc. NH ₄ OH, 1 cc. NH ₄ Cl, diluted to 100 cc.
" III.	75 cc. phenolphthalein, 1 cc. NH ₄ OH, 2 cc. NH ₄ Cl, diluted to 100 cc.
" IV.	75 cc. phenolphthalein, 1 cc. NH ₄ OH, 2.5 cc. NH ₄ Cl, diluted to 100 cc.
" V.	75 cc. phenolphthalein. 0.8 cc. N Na H, diluted to 100 cc.

$\lambda = \text{A.U.}$	I.	II.	III.	IV.	V.
5773	48.2	62.2	73.0	81.3	15.7
5798	54.2	66.3	78.7	83.0	22.7
5823	59.6	70.7	83.9	86.0	30.5
5848	66.4	74.6	85.1	89.0	37.9
5948	84.8	87.7	—	94.8	62.2

TABLE XIV.

Solu- tion.	$\lambda =$ A.U.	Lactoid form. $c \times 10^5$.	Quinoid salt. $c \times 10^5$.	OH $\times 10^5$.	K_{10}/K_1 $\times 10^5$.	$K_1 \times 10^{10}$.
I.	5773	2.09	1.36	5.039	7.79	1.04
	5798	2.03	1.42	5.039	7.24	1.12
	5823	1.95	1.50	5.039	6.56	1.23
	5848	1.99	1.46	5.039	6.92	1.17
			average ..			1.14
II.	5773	2.56	0.884	2.519	7.31	1.11
	5798	2.49	0.953	2.519	6.61	1.23
	5823	2.44	1.006	2.519	6.13	1.32
	5848	2.41	1.040	2.519	5.83	1.39
	5948	2.49	0.951	2.519	6.61	1.23
			Average ..			1.25
III.	5773	2.86	0.587	1.259	6.15	1.32
	5798	2.89	0.557	1.259	6.53	1.24
	5823	2.94	0.508	1.259	7.96	1.02
	5848	2.87	0.573	1.259	6.37	1.27
			Average ..			1.21
IV.	5773	3.05	0.386	1.007	8.03	1.01
	5798	3.01	0.433	1.007	7.01	1.15
	5823	3.01	0.436	1.007	7.01	1.15
	5848	3.03	0.413	1.007	7.42	1.09
	5948	3.06	0.385	1.007	8.04	1.01
			Average ..			1.06

The series of solutions, the results of which are recorded in Table XIII., were prepared from another solution of phenolphthalein. Its concentration was 4.603×10^{-5} grm.-molecules per litre. The concentrations of the ammonium hydroxide and ammonium chloride solutions were the same as for the previous series. It will be noticed that 1 cc. of a solution of ammonium hydroxide was used instead of 2 cc. as in the former case.

(To be continued).

THE TOWER SYSTEMS OF MAKING SULPHITE ACID.*

In continuation of an article on "Technology of the Sulphite Pulp Process" reproduced in a recent number of the *Chemical Engineer* from the *Pulp and Paper Magazine*, G. B. Steffanson proceeds to discuss the tower systems of manufacturing "sulphite acid." The high tower system, he says, apparently displacing all other systems in Europe, and even on this continent it appears to be gaining much ground.

The high towers are more expensive to instal than any of the other systems, and the running cost is somewhat higher because the limestone must be hoisted to the top of the tower for charging, but they offer many advantages in other directions. The acid or gas does not come into contact with any pumps or valves before it is ready to be conveyed into the storage tanks, and therefore many costly repairs and renewals are avoided.

The system consists of four or more round tanks, 100 to 120 ft. high or even higher, usually 8 to 10 ft. in diameter, made of hard acid-resisting wood. The tanks are slightly tapering upwards, and are lined with acid-resisting brick or boards, in order to avoid wear and tear of the tanks by the limestone.

The tanks are joined, and surrounded with a wooden structure, to form a tower, divided into a convenient number of floors, from which the tanks can be entered if this should prove necessary. The different floors are connected with the ground and with the top floor by means of stairs and a limestone hoist, as well as a passenger lift.

A water tank is placed on the top of the tower, which should be of sufficient capacity to supply the tower with water for a few hours, in case the water supply should break down. The water in this tank is also used for washing out the tanks periodically in order to free them from materials which might spoil the draught. This tank is, if possible, supplied with spring water, by means of a pump. This pump, and the hoist and lift, are the only pieces of machinery in connection with the tower.

The high tanks act as smokestacks and no forced draught is required unless pyrite burners are used.

The water is distributed over the limestone in the tanks in suitable quantities by means of sprinklers or other arrangements, so that it is evenly distributed and drips down through the limestone and keeps the surface of this moist.

The limestone in the tanks, which should vary in size from pieces the size of a coconut to a large cabbage, is supported on stout oak beams about ten feet from the bottom of the tanks. A number of beams placed close together are provided about one foot above the outlet for the acid, in order to catch the smaller pieces of limestone falling through the upper coarser grates and hold them till dissolved.

The water trickles down over the limestone and dissolves the SO₂, which then dissolves the limestone, finally forming the acid bisulphite solution of the composition already mentioned.

The cooled SO₂ is distributed to the different tanks by

* *Chemical Engineer*, xxi., No. 6. (Reprinted from *Paper*).

means of lead pipes fitted with water seals, so that any one of the tanks can be disconnected from the system. The acid overflows a few feet from the bottom of the tanks into a settling tank, and is finally pumped or run by gravity into the storage tanks.

The bottoms of the tanks are made to slant towards the mudholes, which should discharge into a sewer, and at the mudholes are usually arranged waterpipes with sprays, in order to prevent the odour of SO_2 when the sludge is washed out.

This washing-out must be done at intervals of from one to four weeks, varying with the purity of the limestone and the design of the tanks, in order to prevent too much sludge from going into the settling and storage tanks. When this tower system is used, the escape of SO_2 at the top of the tower should be carefully controlled, especially in summer time and when cold spring water is not used; the water supply to the tanks should be adjustable from the bottom of the tower.

Low Tower System Cheaper.

The system of low towers, 35 to 50 ft. high, with four or more round or square tanks, connected as previously described, is cheaper in first cost but presents many disadvantages. Two tanks are worked together in such a way that the gas rises through the first tower and is passed to the bottom of the second tank through earthenware pipes and finally goes up this tower. In order to obtain the necessary draught the tanks must be closed at the tops and a fan or steam ejector provided on top of the second tank. The weak acid from the second tower is pumped to the first tower. The machinery required for the system is costly to maintain in good order. In these towers the limestone usually rests on beams on the level of each floor of the tower, and the charging done from the different floors. This increases the cost of charging and cleaning considerably.

The charging cannot be done every day, but at intervals of one or two weeks, and thus the acid contains too much lime immediately after charging the tanks, and is deficient in lime before charging, unless the mill is so large that several systems of tanks are in use, when this unevenness of the lime in the acid is eliminated. With regard to water supply, gas connections, acid connections, and settling tanks, the low towers are arranged in the same way as the high towers.

Instead of using towers, four or more tanks can be connected in series, as described in connection with the low towers. This system is very expensive in upkeep, and is in use in only a few of the oldest mills in Europe.

The Chamber System.

The cheapest limestone system of all as regards first cost is the chamber system. If the waste gases can be taken to a chimney each system only requires two phosphor-bronze pumps. The apparatus consists of two long, square chambers which are built together and connected, and each divided into eight or more compartments, connected alternately at the top and at the bottom. This system is not automatic. In one chamber a certain quantity of water is admitted, and the other chamber contains weak acid. The gas is drawn down through the next one, and then in the same way first through the chamber containing the weak acid so that it passes up through one compartment and through the second chamber, containing the water. Each chamber has a circulating pump, which takes the liquid from the bottom of the chambers through a pipe with branches going into each compartment. The liquid is spread over the whole of the compartment by means of sprinklers and trickles down through the limestone, which rests on grates a few feet above the surface of the liquid.

When the acid in the first chamber is strong enough, it is drawn off and water admitted. The gas is then drawn through the system in the opposite direction, *i.e.*—again first through the weak acid and then through the water.

The reversing arrangements should only be watersealed, as the necessary suction is only $\frac{3}{4}$ in. of water or slightly more. In a few Scandinavian mills, chamber systems with three chambers are used, and some of the mills work them continuously, in which case it is necessary to add a gas saver so as not to lose too much gas.

Milk of Lime Systems most usual here.

The milk of lime systems consisting of closed tanks are the most usual on this continent, but they are used in very few mills in Europe. They all work on the principle of drawing the gas through one or more tanks nearly full of liquid, in which the SO_2 is absorbed and the lime dissolved. These tank systems are undoubtedly the cheapest of all acid-making apparatus from the point of view of first cost, and are very easy to handle, but show several disadvantages. The cost of burning the lime has already been mentioned. The vacuum required is considerable amounting to more than the combined height of the liquid in the tanks, and the air pumps are large, and need considerable maintaining in order to work properly. The tanks and connections must be kept perfectly airtight. The systems are usually difficult to adjust with regard to the quantity of acid made, except within narrow limits, and interruptions in the run cause large losses.

There are three essentially different types—namely, Burgess', Stebbins', and Barker's systems. The Burgess apparatus is usually made in the form of one high tank, which is divided into three parts by means of horizontal partitions. The tank is fitted with a stirrer with hollow shaft and arms. The gas passes through the shaft and the perforated hollow arms into the lowest compartment, and then in the same way up to the upper compartments, being intimately mixed with the liquid when the arms of the stirrer pass through it. Stebbins' apparatus consists of two or more tanks usually arranged in steps, and provided with stirrers and two or more partitions in each tank with holes so arranged that the gas which is drawn in at the bottom, must pass from one side of the tank to the other, so as to come into as intimate contact as possible with the liquid in the tanks. Barker's apparatus consists of a high tank provided with three or more horizontal perforated partitions. The gas is drawn in at the bottom and passes up through the liquid and the perforated partitions.

All these systems are provided with overflow pipes for the acid from a higher tank or compartment to a lower one, and the gas pipes are U-shaped to prevent acid from being drawn from a higher tank to a lower one through these pipes. Milk of lime is admitted continuously to the top tank, and in such quantities that the acid flowing from the bottom tank is clear—*i.e.*, all the lime is dissolved. The composition of the acid is regulated by the quantity of lime charged in the milk of lime tank; care should, however, be taken that the milk of lime is not too rich in lime, in which case large quantities of SO_2 will escape through the suction pumps or ejectors if the acid is run clear.

Low towers for milk of lime are in use in only a few mills in Europe. The system consists of three or more towers of 25 to 40 ft. high, connected in series, and each provided with a covered feed tank with stirrer and pump. Artificial draught, giving a vacuum of 3 to 4 in. of water is necessary, and is usually created by means of a fan or a steam ejector. The towers are fitted with stones or pieces of wood, so as to provide a large area of contact for the liquid and the gas. The disadvantage of this system is that the tanks become clogged with calcium sulphate, and the cleaning is expensive, and requires much time, as the gypsum sticks to the filling materials.

Several combinations of the above systems are also in use, but it is outside the scope of this article to discuss them.

When using milk of lime systems for manufacturing

acid, it is very important to slake the lime properly. Two methods of slaking are in use. The quicklime is dumped into tanks filled with water provided with agitators, and the liquid is heated to boiling. The milk of lime is then screened before it is passed into the storage tanks. By the other method the lime is slaked in kollergangs or troughs, with the minimum quantity of water, and is then washed into the storage tanks over wire screens and diluted to proper consistence. The second method requires more labour but saves lime and steam. Milk of lime should always be stored in such quantities that it has time to cool down before being admitted into the acid apparatus, as the absorption of SO_2 by the water diminishes very rapidly with increasing temperatures. The storage tanks for milk of lime should always be provided with efficient stirrers.

The acid storage tanks should be so arranged that any leaks can be readily detected. The tanks should also be covered and fitted with gas pipes leading into the acid-making system, or to the gas reclaiming plant if more convenient.

The acid storage tanks may be made of concrete, sheet iron, or wood-lined, with acid-resisting brick, or even common red brick, well pressed and burnt, set in acid-proof mortar, and with or without a lead lining behind the bricks. Tanks made of hard pine are cheap, and can be used for many years without lining; they can later be lined with brick and acid-proof mortar.

If possible a 24-hour or more supply of acid should be stored, and the storage tanks should be so arranged that the raw acid coming from the acid-making plant can be blown with SO_2 from the relief and blowing off of the digesters, before it is mixed with the finished cooking acid.

In this connection may be mentioned the cooling of the gas from the digesters, before it is blown into the acid. The cooling of the gas has to be carried far enough to prevent the temperature of the acid from rising to more than 120°F. , otherwise calcium sulphite may separate. The gas pipes from the coolers should be so arranged in the bottom of the blowing storage tank as to produce circulation of the acid, in order to prevent overheating of any part of the acid.

On the other hand the acid should be heated by the gases from the digesters to at least 100°F. in order to save steam.

The gas coolers are either made in the form of lead coils in circular tanks, or an elongated system of pipes of the same diameter as the relief pipes from the digesters, laid in a shallow trough.

Water is preferably and almost exclusively used for the purpose of cooling the gases; only a few old Mitscherlich mills still use the original air-cooling in long cast-iron pipes.

The raw materials used in the manufacture of acid should all be tested by a skilled chemist, and any leakage of gas should be carefully guarded against. The escape of any SO_2 from the acid-making apparatus should be carefully checked, or else great waste may occur.

For an economical running of the plant supervision in other directions is also essential. The burning of the sulphur should be complete combustion, without a large excess of air being admitted. The pyrite burners should always be kept perfectly airtight except for the proper inlet of air.

The composition of the gas should be ascertained and the cooking acid should be blown to its correct temperature and composition.

The composition of the waste gases leaving the acid system can be periodically followed by means of Orsat's apparatus or other apparatus constructed for the purpose. The gas coming from the burners should also be analysed.

It is essential to arrange automatic self-registering instruments in all places where the content of SO_2 in the gas has to be ascertained. An excess of air in the SO_2 gas causes difficulties, because the moisture in the air ad-

mitted, as well as that in the sulphur or pyrite, forms steam in the burners, which causes the formation of sulphuric anhydride (SO_3), which in contact with lime (CaO) forms gypsum (CaSO_4). The insoluble gypsum causes deposits and clogging, particularly in limestone systems, and this causes considerable loss of sulphur and lime. This trouble seems to have made the limestone systems unpopular when first used on this continent. The gas from the burners in plants which are run carelessly contains frequently only 7 to 8 per cent of SO_2 . The content of SO_2 in the gas should not fall below 12 or 14 per cent for pyrite burners, and can under favourable circumstances amount to 16 or even 18 per cent in gas from sulphur burners. The theoretical amount of about 21 per cent cannot be obtained without sublimation of sulphur and subsequent clogging of the coolers and waste of sulphur.

Sublimation may occur even with a low proportion of SO_2 in the gas if the temperature in the burner is too high and no secondary air is admitted behind the burners, so as to promote the combustion of the sublimed sulphur in the combustion chamber.

It is of great importance where milk of lime systems are used to keep the composition of the acid constant, both when it comes from the acid apparatus and when it has been blown with gas from the digesters. It has in most of these systems proved impossible to make an acid of proper strength without considerable loss of SO_2 , and to remedy this separators have been used to separate condensed steam from the SO_2 gas coming from the digesters, and in this way get the blown acid up to proper strength.

In limestone systems this is not necessary. The ratio of free and combined SO_2 should here be kept constant, and the acid should be made so strong that after blowing with the cooled gases from the digesters without previous separation of condensed steam it should be of proper strength for cooking, or stronger, as it is easy to dilute it.

In order to get a uniform pulp and not waste chemicals the digesters should always be charged with the same quantity of free and combined SO_2 , and not, as is very often the case, charged with a certain quantity of acid regardless of its composition.

Green wood needs a somewhat stronger acid than dry wood. Care should be taken, however, that enough acid is charged to prevent burning of the chips in the upper part of the digester.

(To be continued).

PROCEEDINGS OF SOCIETIES.

ALCHEMICAL SOCIETY.

TRANSCENDENTAL ALCHEMY.

THE Twenty-second General Meeting of the Alchemical Society was held on November 12 at 22A, Regent Street, S.W. The Chair was occupied by the Acting President, Mr. H. STANLEY REDGROVE, B.Sc. (Lond.). F.C.S.

A revised set of rules, drawn up by a special committee appointed by the Council, were approved and adopted. The annual subscription is thereby increased to 12s. 6d., the Council is empowered to elect honorary members, and one or two other minor alterations have been made.

The latter part of a paper by the late Mrs. Atwood, authoress of "A Suggestive Enquiry into the Hermetic Mystery and Alchemy," presented to the Society by Mme. Isabelle de Steiger, and edited by her, was read. Mrs. Atwood's paper dealt with Alchemy as a psychological process wrought by man, on the assumption that the old alchemical writers clothed their meaning in symbolic language. The former portion of the paper was read at the preceding meeting of the Society.

A discussion was held in which the question of the validity of so translating the alchemical text was raised,

and also the question of the significance of water divining, hypnotism, and allied phenomena on the assumption of Mrs. Atwood's theory.

NOTICES OF BOOKS.

Qualitative and Volumetric Analysis. By W. M. HOOTON, M.A. (Oxon.), M.Sc., F.I.C. London: Edward Arnold. 1915.

THIS book gives first an ordinary course of work in qualitative analysis, beginning with dry tests, then passing on to the metals in solution and the acid radicles, and finally giving separation tables. Although the directions are concise and the matter is well arranged there appears to be no particular novelty in the treatment. A good feature is the inclusion of the rarer metallic ions, such as tungsten, vanadium, &c., which are of considerable technical importance, and the reactions of the less common acid radicles as well as some organic acids are also tabulated. The principles of volumetric analysis are clearly explained, and a good selection of examples and additional exercises is provided.

Quantitative Law in Biological Chemistry. By SVANTE ARRHENIUS, Ph.D., M.D., LL.D., F.R.S. London: G. Bell and Sons, Ltd. 1915.

THIS book is based upon three Tyndall Lectures, delivered by the author at the Royal Institution in May last year. It contains descriptions of the author's pioneering work on quantitative measurements in biochemistry, with discussions of the conclusions to be drawn from it and the experiments of other investigators in the same sphere. Velocity of Reactions, the Influence of Temperature on the Velocity of Reactions, Reactions of Cells, Quantitative Laws of Digestion and Resorption, Chemical Equilibria and Immunisation are the titles of the chapters, and the book may be said to treat of vitalism from the chemical standpoint and to discuss the applicability of the physico-chemical laws of general chemistry to biochemical processes. The methods and theories of physical chemistry are of very great importance for the development of an exact science of biochemistry, and this book contains an excellent summary of the work that has already been done, and should prove both interesting and stimulating to students of the science.

John Dalton's Lectures and Lecture Illustrations. Parts I. and II., by Prof. W. W. HALDANE GEE, B.Sc., M.Sc.Tech. Part III., by HUBERT FRANK COWARD, D.Sc., and ARTHUR HARDEN, D.Sc., Ph.D., F.R.S. Manchester: 36, George Street. 1915.

THESE extracts from the memoirs of the Manchester Literary and Philosophical Society contain descriptions of some diagrams made and used by John Dalton, which were found in a cupboard in the house of the Society. The diagrams, after they had been examined by experts, were cleaned and repaired, and this catalogue of them was prepared. In all they number about 150, and they were divided into two groups; firstly, those relating to Mechanics, Physics, Astronomy, and Meteorology, and secondly those dealing with the Atomic Theory. These latter, which are described in Part III. of the pamphlet, are particularly interesting. Short summaries of some of the lectures are included, prepared from lecture notes and syllabuses of courses of lectures, which were found among the Dalton manuscripts and miscellaneous packets of papers.

Literary Intelligence.—Messrs. J. and A. Churchill announce the publication of the following new books:—"An Introduction to the Physics and Chemistry of Colloids," by Emil Hatschek; Second Edition, with 17 illustrations; price 3s. net. "Catalysis and its Industrial Applications," by E. Jobling, A.R.C.Sc., B.Sc., F.C.S.; with 12 illustrations; 2s. 6d. net.

CORRESPONDENCE.

PREPARATION OF SULPHURETTED HYDROGEN.

To the Editor of the Chemical News.

SIR,—The following description of a simple apparatus for the preparation of sulphuretted hydrogen and similar gases, which I devised after much trouble with Kipp's and other forms may be of use to your readers.

An efficient and easily cleaned apparatus for the preparation of sulphuretted hydrogen and similar gases may be made by using for the generating chamber a calcium chloride drying tower. In the constricted part near the bottom is placed a short piece of glass rod of nearly the same diameter and with a flattened head just large enough



to prevent it falling through. In the head channels are cut with a file or pressed while hot. This support permits the use of iron sulphide in small pieces, with which the tower is nearly filled. Acid is admitted through the tubulure, easily enters the generating chamber, and, meeting with a large surface of sulphide, quickly produces a copious current of gas, which, having very little space to fill in the tower, is at once available for use.—I am, &c.,

HAROLD ELLIS

Chemical Laboratory, Leeds Forge,
Leeds, October 31, 1915.

MEETINGS FOR THE WEEK.

WEDNESDAY, 24th.—Royal Society of Arts, 4.30. "Constantinople, Ancient and Modern," by Sir Edwin Pears.

THURSDAY, 25th.—Royal Society. "Measurement of the Rate of Heat Loss at Body Temperature by Convection, Radiation, and Evaporation," by M. Flack, O. W. Griffith and L. Hill. "Rate of Absorption of various Phenolic Solutions of Seeds of *Hordeum vulgare* and the Factors governing the Rate of Diffusion of Aqueous Solutions across Semipermeable Membranes," by A. J. Brown. "The Controlling Influence of Carbon Dioxide—Part III., The Retarding Effect of Carbon Dioxide on Respiration," by F. Kidd. "Growth of the Body in Man—The Relationship between the Body Weight and the Body Length (Stem Length)," by E. W. A. Walker.

THE CHEMICAL NEWS.

VOL. CXII., No. 2922.

THE SOLIDIFYING AND MELTING-POINT OF ANETHOL.

By ROBERT MELDRUM

ANETHOL is a very useful and convenient substance for investigating melting- and solidifying-point methods, as it is strongly crystalline and melts at ordinary laboratory temperatures. The majority of melting- and solidifying-point methods evolve the use of water-jackets, air-jackets, or a combination of these in laboratory air temperatures considerably lower or higher than actual melting-point. As the author has previously shown (CHEMICAL NEWS, 1915, cxi., 95) solidification can take place in surface layers due to contact of cold air with surface of melt yielding high results. There is no doubt that temperature of atmosphere in which solidification or melting takes place in many cases modify these points the more so the greater the ratio between laboratory temperature and melting-point. Substances therefore like anethol, which melt at ordinary room temperatures, are valuable for investigating conditions which govern erratic solidification. Anethol is stated by Allen to melt at 20° C., which is about 4° higher than the author's results. The tube used in the following tests was $\frac{3}{4}$ inch diameter, unless otherwise stated. The thermometer being 50° C. divided into tenths. The anethol was, so far as could be ascertained, pure, and was purchased as such with declared melting-point 21° to 22° C.

Melting-point.

Thermometer Bulb Method.—Cooled down thermometer to 0° C. and dipped rapidly into liquid anethol at 12° C. to obtain coating, and allowed to melt in laboratory temperature at 16° C. The following are the results (°C.):—

15.7 15.8 15.7 15.9 15.8

Opacity Method.—Solidified anethol in test-tube at 9° C., and placed in water-jacket at 14° C. and raised temperature jacket at about 1° C. per fifteen minutes with constant stirring of anethol and jacket. The melting-point is when all traces of opacity disappears

Temperatures °C.
Room. Jacket. Anethol.

13	17	16	Thin opaque paste.
13	18	17	Transparent limpid liquid.
16	15.5	15.5	Anethol solid.
16	16	16	Very soft paste drips off bulb.
16	16.5	16.5	Opaque liquid.
16	16.8	16.8	Transparent, all melted.

Ten determinations by this method gave 17° C. as melting-point. At 17°, though all in tube is melted, a thin ring of solid above surface of melt and adhering to side of tube does not melt, but does so at 18° C. At 17° C. the melted anethol in each test still retains a trace of finely-divided crystals in suspension.

With spermaceti, tallow, stearic acid, thymol, menthol, anethol, and many other substances higher melting-points are obtained by this method than by the thermometer bulb method. This is no doubt due to the enormous difference between the quantities employed in each case. With all these substances a trace of suspended finely-divided crystals persist at the actual melting-point, and in some cases 1° and 2° above it, and this, as will be shown, has a powerful effect in producing erratic solidification.

Solidifying-point.

Method A.—Constant stirring in air-jacket. Stirred till rise commences and fixed thermometer for reading.

T° air, °C.	..	..	..	8	9	10	10.5	10.5	12
Solidifying-point + rise, °C.	15	15.6	15.4	15.5	15.3	15.4			
Rise, °C.	..	..	..	6	2	5.4	4.7	2.6	3.4

Average solidifying-point 15.36° C.
Variation " " 0.60° C.

At 10° C. the anethol requires in some cases ten minutes stirring to solidify. In other cases instantaneous solidification takes place at this temperature. This, it was observed, depends upon the previous temperature at which the solid anethol was melted. If both thermometer and anethol have been at a temperature of 20° C. for ten minutes this causes all traces of floating crystals to melt, and lower supercooling is required to start solidification. On the other hand, if the anethol has only been melted at 17° C. solidification commences with little supercooling due to the presence of this finely-divided solid matter. The highest "rise" gives the lowest result, and *vice versa*. The air temperatures prove that these have no effect on erratic solidification.

Method B.—Constant stirring in cold water-jacket. Stirred anethol till temperature began to rise, and fixed thermometer for readings.

T° air, °C.	T° water-jacket, °C.	T° anethol, °C.	S.P. + rise, °C.	Rise, °C.
20	4	7	14.3	7.3
20	8	8	14.7	6.7
20	12	11	(a)	(a)
13	12	13	(a)	(a)
20	11	11	(a)	(a)
20	3	6	14.1	8.1
20	7	7	14.3	7.3
14	3	7	13.5	6.5
14	8	8	13.8	5.8

Average solidifying-point 14.1° C.
Variation " " 1.2° C.

(a) No solidification.

The three tests which failed to solidify is due to insufficient supercooling and melting above 18° before cooling. None of these solidify at the above temperatures after thirty minutes stirring. When the anethol is melted at 17° C. the following results were obtained:—

T° water-jacket, °C.	14	14	14	13
T° anethol, °C.	..	14	13	12
S.P. + rise, °C.	..	15.7	15.7	15.5
Rise, °C.	..	1.7	2.7	3.5

Average solidifying-point 15.5° C.
Variation " " 0.5° C.

In these experiments, it was observed, traces of finely-divided crystals were suspended in the melt, and this again points to the fact that melting above melting-point induces supercooling with low solidifying-points, but melting at melting-point yields high solidifying-points. This explains to some extent many obscure phenomena relating to solidification in general, and also variation in the solidifying-point.

Method C.—Melted at 17° C. till about 2 per cent remains unmelted, stirred in air jacket till solidification commences, and fixed thermometer for readings.

T° air jacket, °C.	..	7	8	9	10	13	14
T° anethol, °C.	..	14	13.5	13.2	13.5	14.5	14.5
S.P. + rise, °C.	..	14.5	14.5	14.6	14.7	15.1	14.9
Rise, °C.	..	0.5	1.1	1.4	1.2	0.6	0.4

Average solidifying-point 14.7° C.
Variation " " 0.6° C.

The rise here is very slow and requires thirty minutes to complete. At the end of the rise a soft solidification results. The thermometer then remains stationary for twenty minutes, at the end of which the solidification is almost rigid. Under these thermal conditions, when the rise is completed the mass is a mixture of about 20 per cent solid anethol and 80 per cent liquid anethol, as at these stages when all is stirred the crystals precipitate, leaving about 1 cm. liquid on top. In about fifteen to thirty minutes all becomes a hard, solid mass. From observations made it was seen the speed of crystallisation was far from being regular, which appears to be the main factor in causing variation in results. The most prominent fact brought out is that even in the presence of solid anethol, as to be expected, low supercooling results but high solidifications are not obtained.

Solidification in Tube 1 inch Bore.

(Melted at 17° C. Solidification in air-jacket).

T° room, °C.	..	12	12.5	11	10.5	9.5
7° anethol, °C.	..	13	13	14	12	13.9
S.P. + rise, °C.	..	14.6	14.8	14.8	14.8	14.7
Rise, °C.	..	1.6	1.8	1.8	2.8	0.8

Average solidifying-point 14.7° C.
Variation " " 0.2° C.

From the above it will be seen diameter of tube does not affect solidifying-point, as with thymol. When thermometer has ceased to rise the solidification is very soft and contains much liquid anethol, as this is easily pressed out with thermometer. The rise takes about twenty minutes and then remains stationary for another twenty minutes, and thence thermometer commences to fall at the rate of 0.1° C. per ten minutes. This is due to liquid anethol dispersed through the crystals solidifying with lowered temperature. At 0.3° C. below maximum rise the solidification is quite hard, rigid, and opaque, and no liquid anethol can be pressed out. On revolving thermometer in the mass no further rise, as in the case of menthol, takes place.

Solidification of Anethol in Bulk.—200 grms. anethol in stoppered bottle, with laboratory temperature at 10° C. for several hours, a thick layer of crystals form on top and some on bottom. On stirring anethol registers 13.8° C., and on fixing thermometer rises to 14.7° C. which is a mixture of liquid and solid, which gains in solidity on standing, with thermometer still at 14.7° C.

Solidifying-point Lowered by Ageing.—Keeping anethol in stoppered bottles for five months exposed to light in a room temperature of 15° to 20° C., the solidifying-point falls to 5.5° C., as follows:—

Anethol cooled, °C.	..	0	2	3	2
S.P. + rise, °C.	..	5.5	5.4	5.5	5.3

On heating anethol to 110° C. for twenty minutes to expel moisture the solidifying-point remains unchanged. This lowering of the solidifying-point by ageing is no doubt due to absorption of oxygen by anethol.

Summary.

The solidifying-point has been found to vary from 13.5 to 15.9° C. by the various methods used, a difference of 2.4° C., the cause of which is erratic solidification, due mainly to melting the anethol a few degrees above melting-point, which induces supercooling. Omitting the results obtained by Method B, the difference in all the remaining twenty-two determinations agree within themselves by 1.2° C. The solidifying-point, therefore, of this particular sample of anethol varies between 14.5 and 15.7° C., which is in close agreement with melting-point by thermometer-bulb method, 15.8° C. The disturbance of room temperature so far as these experiments go is very little or nil.

INTRODUCTION TO THE THEORY OF RELATIVITY.

By F. H. LORING.

(Concluded from p. 250).

LET US now reconsider the whole relativity matter from the point of view as suggested by Mr. Wells' little novel, "The Time Machine."

Mr. Wells says that an instantaneous cube, a figure of three fundamental dimensions, has no real existence, and we must therefore take into consideration *duration* or *time*, which becomes a *fourth dimension*.* From one point of view, we might therefore consider that the mathematics involving a fourth-dimensional axis is, as it were, *substantialised*, since we associate reality with substance, an idea Minkowski introduced in his work, and which might be referred to as *Minkowski's four-dimensional world*. Mr. Wells goes on to say (see foot-note) that our consciousness moves along *with time*; this, then, means that we can cancel out the time concept, because, if we move along with a thing we cannot realise that it is in motion. We must of course assume an ideal or perfect case. This leaves us with *three-dimensional mathematics* of old, which is not a *substantiality* in the sense intended. The motions taken in all these cases are rectilinear and uniform.

We then proceed to eliminate or correct our consciousness, as it were, when we come to consider phenomena from a different aspect, or from a *new relativity* point of view, and thus our fourth-dimensional idea of time is reinstated; † concurrently with this, however, we have to consider the phenomenon as something that appears differently to different observers, *if they are in different relative movement with respect to the thing observed* (to take a particular case); hence our phenomenon is not *real* in the sense that it was before our mathematics had assumed a substantial-like aspect.

It is well to realise, by way of example, that "what to a stationary observer is an electrostatic field, is an electromagnetic field to a moving observer," and this implies the attachment of a deeper meaning to the word *appearance*, or its equivalent, since the different effects are measurable with apparatus. Moreover, they are respectively only real in that they are *statically* real, or *relatively* real, according to circumstance, and the two concepts *real* and *abstract* (if this word may be thus used) as applied to mathematics are likewise interchangeable according to circumstance (see article on "Mass, Weight, and Electrical Inertia," CHEMICAL NEWS, 1915, cxii., 99). It must also be realised that time and space are bound up together, being part and parcel of each phenomenon.

Cunningham (*loc. cit.*, 217), in his concluding remarks says:—"In spite of all the elaborate structure of mathematical developments which has been built up in connection with the principle, the most important aspect of it is still that which, with a flash of insight, was first enunciated by Einstein, the assertion that metrical space and time are not independent and self-contained concepts, but that they are conditioned by the very phenomena which they are used to describe. Though now to many this seems an obvious truth, and though it has been implicit in the way in which many thinkers have always looked upon the meaning of all physical measure-

* Mr. Wells says:—"Can an instantaneous cube exist? . . . 'Can a cube that does not last for any time at all have a real existence?' . . . 'Clearly . . . any real body must have extension in four directions; it must have Length, Breadth, Thickness, and—Duration.' . . . 'There is no difference between Time and any of the three dimensions of Space except that our consciousness moves along with it.'"

† Cunningham (*loc. cit.*, p. ix.), says:—"The consciousness of space and time are eliminated in conducting exact measurements, so that the measures of space and time are conditioned by the phenomena which they are used to describe."

ments, yet the point of view is still far from being generally adopted." (The heavy-faced type is mine).

There is another feature that cannot be more aptly described than by quoting from the review referred to above. "Some of the most remarkable results of the relativity theory are contained in the chapter on the composition of velocities. The theory does not modify by appreciable terms our classical Newtonian formulæ as long as the ratios of the velocities in question to that of light are small, but when the ratios approach unity entirely new formulæ must be used for compounding velocities, which are such that if an observer measures the velocities in opposite directions of two different bodies relative to himself, no matter how near the velocity of light these may be, the velocity of the one body as measured by an observer of the second will still be less than that of light. In fact, a relative velocity greater than that of light is impossible, in so far as it cannot be dealt with by the relativity theory, which is based upon the use of light signals."

In considering the Newtonian dynamics in the light of relativity, it seems to me we forget the case of the heavenly bodies, for example. Their velocities are not comparable to that of light, but they possess individually enormous masses. From a momentum point of view we do not ordinarily distinguish between mass-magnitudes (m) and velocity-magnitudes (v); v may be very small and m very large, or *vice versa*. According, however, to the relativity idea, we should have to make a distinction; we could not interchange the magnitudes and get the same momentum, especially in extreme cases where, for instance, v approaches that of light. Moreover, we talk about very great velocities of matter, but surely we must remember that matter is only moved by force, and we have concentrations of force which reach limits, so that to talk about a body moving without considering the force producing, or having produced, the movement is in a sense absurd, and this brings us at once to the rationale of the Newtonian dynamics. If we could move ponderable matter with the velocity of light, possibly we should have to consider an intensity of force greater than that of atomic explosions in radio-active phenomena. In other words, we should be considering a dynamical impossibility, just as in relativity a velocity greater than that of light becomes impossible of consideration. The idea of a mass-limit is suggestive in this connection when considering the interchange of values. *These are matters, however, that may be fully reconciled by a deeper study of the subject, this being, of course, only a superficial treatment that leaves much to be desired.*

It should be borne in mind that the principle of relativity is rendered difficult to understand, partly owing to the necessity of defining the new ideas in terms of (or from the standpoint of) the old ones, thus introducing some confusion, and partly owing to the apparently artificial constant c being introduced as a sort of standard tool for gauging the relative measurements.

Mathematical methods involving certain transformation equations are also factors from the point of view of electrodynamics, as the theory sprung up in electromagnetic soil, to use a well-known metaphor.

Prof. Richardson's "Electron Theory of Matter" contains much that should be studied. On page 281 he says:

* The velocity of light in moving media and the Doppler effect (an observed shift in the position of the spectral lines due to the light-source moving towards or away from the observer, which means that the light frequency and wave-length are altered correspondingly) have to be considered from the point of view of Einstein's kinematics, which, in the case of the dragging coefficient, leads to Fresnel's famous formula, so that $u + v \left(1 - \frac{1}{n^2}\right)$ = velocity of light in the moving medium; u = velocity of light relative to the medium; v = velocity of the medium; n = refractive index: but see Cunningham's book (*loc. cit.*) pp. 61-62 (and pp. 55-56), for amplified statement.

"We know from the results of Chapter XI. that the field due to an electric system in motion differs from that due to the same system at rest, in such a way as would result if all the lengths parallel to the direction of motion were changed in the ratio of $\sqrt{1 - v^2/c^2}$ to 1. Thus, for the electrical forces to have the same value in the moving as the fixed system it is necessary that all lengths in the former which are parallel to the direction of motion should be reduced in the ratio $\sqrt{1 - v^2/c^2}$ to 1." On page 318 the same author says:—"Thus an addition δE to the energy of any system will give rise to an increase $\delta E/c^2$ in its mass. It is only a short step from this result to the hypothesis that all mass is simply a manifestation of confined energy." This statement is in the "Relativity" subsection—"Inertia of Energy"—and is the outcome of some calculations. He goes on to say:—"The question whether or not mass is simply a manifestation of confined energy is obviously a matter of the very utmost importance, and it is very desirable that it should be submitted to the test of experiment. The energy liberated in chemical actions is so small compared with the 'dead' masses involved that it is hopeless to detect any change of mass thus arising, always supposing that weight as well as mass is proportional to $\mu + E/c^2$ [see original]. In the case of radio-active change the matter is more hopeful. The decrease of mass of a system due to the loss of 1000 grm.-calories is 4.6×10^{-11} grm. Now, 1 grm. atom of radium in radio-active equilibrium evolves about 3.024×10^4 grm.-calories per hour. Thus its diminution of mass per hour would be—

$$\frac{3.024 \times 10^4 \times 4.6 \times 10^{-11}}{9 \times 10^{10}} = 1.4 \times 10^{-6} \text{ mgrm.}$$

This would amount in a year to 0.012 mgrm. or in 100 years to 1.2 mgrms. It would be worth while of anyone who could afford the necessary capital to make observations of this character." This was written before the war, and now "capital" is needed for a better purpose in administering to the needs of humanity. The idea is of interest, and under certain further assumptions there might be a great many "radiums," and consequently an equal number of "leads," but there are other ways of accounting for the observed variation of the atomic mass amongst leads of different origins. (See in this connection CHEMICAL NEWS, cix., p. 241; cx., p. 25; cxi., pp. 13 and 157; and cxii., p. 99). Prof. Richardson, on page 154 (apart from relativity), remarks:—"It is therefore likely that a great many so-called chemical elements are mixtures of atoms having the same chemical properties but differing in mass. The experimentally determined atomic weight is, on such a view, the average of the weights of the constituent atoms, and depends on the relative proportion in which they are present." The above statement regarding the variability of mass as applied to ponderable matter, and apart from the changes in mass due to the α -particles being expelled (subtracted), is obviously too incomplete to carry weight, and the direct experimental evidence so far available is against the idea. We know, however, that the electron does vary in electromagnetic mass (*i.e.*, exhibits variable electrical inertia) in a way which is in accord with the Relativity Theory. It may be that some further circumstance has to be taken into account when dealing comprehensively with ponderable matter, and this theory in its present form then becomes limited to electromagnetic phenomena including light.

Prof. Richardson on p. 7 says:—"Fortunately the two kinds of mass differentiate themselves rather clearly. The mechanical mass is supposed to be independent of the velocity of the body, following the principles of mechanics laid down by Newton, whereas the electromagnetic mass is a continuous function of the velocity and approaches infinity as the velocity of the electric charge approaches that of light." It has been the modern aim of physicists to unify these ideas.

In conclusion, we may note that this theory enters into

consideration when studying the following subjects:—(1) Aberration and (2) Fizeu's experiment, which are simple cases of relative motion; (3) Electromagnetic equations, and (4) the Dynamics of the Electron, or the Electronic Theory of Matter; (5) Energy and Momentum, and in general the extended Newtonian Mechanics. Besides, we have (6) such problems as the "Inertia of Energy" and (7) the question of the "Aether." Mention should be made of (8) "Longitudinal" and "Transverse" Mass, and (9) the Doppler effect. The list may be extended.

STUDIES IN THE STEREOCHEMISTRY OF QUINQUEVALENT NITROGEN.*

RESOLUTION OF THE ASYMMETRIC QUATERNARY AMMONIUM COMPOUNDS.

By SHIGERU KOMATSU.

(Concluded from p. 253).

G. α -Dextro Methyl Allyl Phenyl Benzyl Ammonium Iodide, $(\text{CH}_3)(\text{C}_3\text{H}_5)(\text{C}_6\text{H}_5)(\text{C}_7\text{H}_7)\text{N.I.}$

A. By adding potassium iodide to an aqueous solution of pure α -dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate prepared in the first experiment, α -dextro methyl allyl phenyl benzyl ammonium iodide precipitated as a white crystalline powder, which was separated from the mother-liquor and re-crystallised from an alcoholic solution in a dark place.

The white needle-shaped crystals melt at 135° to 136° with some decomposition, and were found to have the same chemical properties with its inactive isomer.

A solution of 0.1211 grm. substance made up to 25 cc. with alcohol at 25° , gave $\alpha_D 25 = +0.50^\circ$ in a 20 cm. tube; whence $[\alpha]_D 25 = +51.61^\circ$.

B. The pure active iodide also prepared from the active ammonium dextro-camphorsulphonate obtained in the second experiment consists of white needles melting at 135° to 136° .

The specific rotatory powers of the two preparations were determined in the alcohol and chloroform solutions with the following results:—

(a). A solution of 0.1254 grm. substance made up to 25 cc. with alcohol at 25° , gave $\alpha_D 25 = +0.52^\circ$ in a 20 cm. tube; whence $[\alpha]_D 25 = +51.84^\circ$.

(b). A solution of 0.2102 grm. substance made up to 25 cc. with chloroform at 25° , gave $\alpha_D 25 = +0.92^\circ$ in a 20 cm. tube; whence $[\alpha]_D 25 = +58.28^\circ$.

Its analysis gave the result recorded below:—

0.22 grm. substance gave 0.1398 grm. AgI.

Iodine calculated for $\text{C}_{17}\text{H}_{20}\text{NI}$ 34.79

Iodine found 34.34

H. γ -Dextro Methyl Allyl Phenyl Benzyl Ammonium Iodide, $(\text{CH}_3)(\text{C}_3\text{H}_5)(\text{C}_6\text{H}_5)(\text{C}_7\text{H}_7)\text{N.I.}$

A. The substance was prepared by the action of potassium iodide upon pure γ -dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate obtained in the first experiment, and that crystallised from alcohol in a dark place, has the same melting point (134 to 135°), crystal line form and chemical properties as those of the α -compound.

The specific rotatory power of the substance was determined in an alcohol solution.

A solution of 0.1254 grm. substance made up to 25 cc. with alcohol at 25° , gave $\alpha_D 25 = +0.64^\circ$ in a 20 cm. tube; whence $[\alpha]_D 25 = +63.64^\circ$.

B. The active iodide obtained from the corresponding active ammonium dextro-camphorsulphonate prepared in the second experiment melts at 135° to 136° in a capillary tube.

Its analysis and polarimetric measurement gave the following results:—

0.2235 grm. substance gave 0.1438 grm. AgI.

Iodine calculated for $\text{C}_{17}\text{H}_{20}\text{NI}$ 34.79

Iodine found 34.68

A solution of 0.1281 grm. substance made up to 25 cc. with alcohol at 25° , gave $\alpha_D 25 = +0.65^\circ$ in a 20 cm. tube; whence $[\alpha]_D 25 = +63.45^\circ$.

A solution of 0.2112 grm. substance made up to 25 cc. with chloroform at 25° , gave $\alpha_D 25 = +1.25^\circ$ in a 20 cm. tube; whence $[\alpha]_D 25 = +73.98^\circ$.

It is noteworthy that the iodide of γ form has a higher specific rotatory power than that of α -form just as γ -dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate has a higher value than the corresponding α -compound.

I. α -Lævo Methyl Allyl Phenyl Benzyl Ammonium Iodide, $(\text{CH}_3)(\text{C}_3\text{H}_5)(\text{C}_6\text{H}_5)(\text{C}_7\text{H}_7)\text{N.I.}$

The substance formed by the interaction of potassium iodide and pure α -lævo methyl allyl phenyl benzyl ammonium lævo-camphorsulphonate, crystallises in white plates from alcohol in a dark place.

It melts at 134° to 135° , and its chemical properties are the same as those of its antipode.

A solution of 0.1047 grm. substance made up to 25 cc. with alcohol at 25° , gave $\alpha_D 25 = -0.43^\circ$ in a 20 cm. tube; whence $[\alpha]_D 25 = -51.34^\circ$.

J. γ -Lævo Methyl Allyl Phenyl Benzyl Ammonium Iodide, $(\text{CH}_3)(\text{C}_3\text{H}_5)(\text{C}_6\text{H}_5)(\text{C}_7\text{H}_7)\text{N.I.}$

The iodide prepared from the corresponding pure γ -lævo methyl allyl phenyl benzyl ammonium lævo-camphorsulphonate, crystallises in white plates melting at 135° to 135.5° , and all other properties are same as those of the α -isomer.

A solution of 0.1062 grm. substance made up to 25 cc. with alcohol at 25° , gave $\alpha_D 25 = -0.54^\circ$ in a 20 cm. tube; whence $[\alpha]_D 25 = -63.14^\circ$.

K. α -Dextro Methyl Allyl Phenyl Benzyl Ammonium Bromide, $(\text{CH}_3)(\text{C}_3\text{H}_5)(\text{C}_6\text{H}_5)(\text{C}_7\text{H}_7)\text{N.Br.}$

By the action of potassium bromide upon pure α -dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate, α -dextro methyl allyl phenyl benzyl ammonium bromide was obtained, which crystallises in colourless rhombic prisms from aqueous alcohol in a dark place, and melts at 155° to 156° . It is more solvent in organic solvents than the corresponding iodide.

0.18 grm. substance gave 0.1054 grm. AgBr.

Bromine calculated for $\text{C}_{17}\text{H}_{20}\text{NBr}$ 25.15

Bromine found 24.75

A solution of 0.1075 grm. substance made up to 25 cc. with alcohol at 25° , gave $\alpha_D 25 = +0.57^\circ$ in a 20 cm. tube; whence $[\alpha]_D 25 = +67.44^\circ$.

A solution of 0.116 grm. substance made up to 25 cc. with alcohol at 25° , gave $\alpha_D 25 = +0.63^\circ$ in a 20 cm. tube; whence $[\alpha]_D 25 = +67.89^\circ$.

L. γ -Dextro Methyl Allyl Phenyl Benzyl Ammonium Bromide, $(\text{CH}_3)(\text{C}_3\text{H}_5)(\text{C}_6\text{H}_5)(\text{C}_7\text{H}_7)\text{N.Br.}$

The substance was prepared by the action of potassium bromide upon pure γ -dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate.

It crystallises in colourless rhombic prisms from aqueous alcohol, and melts at 155° to 156° .

It is soluble in alcohol, acetone, and chloroform.

The analysis of the substance is as follows:—

0.21 grm. substance gave 0.1249 grm. AgBr.

Bromine calculated for $\text{C}_{17}\text{H}_{20}\text{NBr}$ 25.15

Bromine found 25.31

A solution of 0.136 grm. substance made up to 25 cc.

* Memoirs of the College of Science, Kyoto Imperial University, 915, i., No. 3.

with alcohol at 25°, gave $\alpha_D^{25} = +0.89^\circ$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +81.80^\circ$.

A solution of 0.11 grm. substance made up to 25 cc. with alcohol at 25°, gave $\alpha_D^{25} = +0.77^\circ$ in a 20 cm. tube; hence $[\alpha]_D^{25} = +82.95^\circ$.

***a*-Lævo Methyl Allyl Phenyl Benzyl Ammonium Bromide**, $(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N.Br.$

The bromide obtained from *a*-lævo methyl allyl phenyl benzyl ammonium lævo camphorsulphonate consists of colourless rhombic prisms, and its melting-point was found to be 149° to 150° showing the lower value than that of its antipode. Its optical rotatory power was determined.

A solution of 0.1185 grm. substance made up to 25 cc. with alcohol at 25°, gave $\alpha_D^{25} = -0.60^\circ$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -63.29^\circ$.

***a*-Dextro Methyl Allyl Phenyl Benzyl Ammonium mercuric Iodide**, $(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N.I.HgI_2$.

A substance was prepared by the method of Pope and Harvey (*loc. cit.*) by the interaction of equimolecular quantities of pure *a*-dextro methyl allyl phenyl benzyl ammonium iodide and mercuric iodide.

It is soluble in acetone, ethylacetate, and alcohol, and crystallises in yellow plates from ethyl acetate, and melts at 119° to 120°.

A solution of 0.112 grm. substance made up to 24 cc. with ethyl acetate at 26°, gave $\alpha_D^{25} = +0.22^\circ$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +24.56^\circ$.

A solution of 0.1142 grm. substance made up to 25 cc. with ethyl acetate at 25°, gave $\alpha_D^{25} = +0.23^\circ$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +25.17^\circ$.

***P*. γ -Dextro Methyl Allyl Phenyl Benzyl Ammonium Mercuric Iodide**, $(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N.I.HgI_2$.

The substance was prepared from γ -dextro methyl allyl phenyl benzyl ammonium iodide and mercuric iodide, and crystallises in yellow plates from ethyl acetate. Its melting-point was found to be 120° to 121°.

A solution of 0.123 grm. substance made up to 25 cc. with ethyl acetate at 25°, gave $\alpha_D^{25} = +0.39^\circ$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +39.63^\circ$.

A solution of 0.1006 grm. substance made up to 25 cc. with ethyl acetate at 25°, gave $\alpha_D^{25} = +0.32^\circ$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +39.39^\circ$.

***Q*. *a*-Lævo Methyl Allyl Phenyl Benzyl Ammonium Mercuric Iodide**, $(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N.I.HgI_2$.

The substance prepared from the corresponding iodide by the usual method consists of yellow plates. It is soluble in alcohol and ethyl acetate, and melts at 119° to 120°.

A solution of 0.114 grm. substance made up to 25 cc. with ethyl acetate at 25°, gave $\alpha_D^{24} = -0.22^\circ$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -24.12^\circ$.

***R*. γ -Lævo Methyl Allyl Phenyl Benzyl Ammonium Mercuric Iodide**, $(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N.I.HgI_2$.

The substance prepared by the action of mercuric iodide upon the corresponding lævo iodide, crystallises in yellow plates from ethyl acetate, and melts at 120°.

A solution of 0.1219 grm. substance made up to 25 cc. with ethyl acetate at 25°, gave $\alpha_D^{25} = -0.39^\circ$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -39.99^\circ$.

***S*. *a*-Dextro Methyl Allyl Phenyl Benzyl Ammonium Chloroplatinate**, $[(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)NCl]_2.PtCl_4$.

The chloride obtained by treating the aqueous solution of pure *a*-dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate with sodium chloride solution was converted into its platinum double salt by the usual method. It crystallises in yellow fine needles from hot aqueous solution, and melts at 149° to 150°.

The substance dried at 100° was analysed.

0.2326 grm. double salt gave 0.0565 grm. Pt on ignition.

Platinum calculated for $C_{34}H_{40}N_2Cl_6Pt.$ 22.08
Platinum found 22.40

***T*. γ -Dextro Methyl Allyl Phenyl Benzyl Ammonium Chloroplatinate**, $[(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N.Cl]_2.PtCl_4$.

The substance was prepared from the chloride formed from γ -dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate, and crystallises in yellow fine needles from hot aqueous solution. Its melting-point was found to be 148° to 149°.

The analytical result of the substance is as follows:—

0.1174 grm. substance gave 0.0264 grm. Pt on ignition.

Platinum calculated for $C_{34}H_{40}N_2Cl_6Pt.$ 22.08
Platinum found 22.49

RADIOMETRIC MEASUREMENTS OF THE
IONISATION CONSTANTS OF INDICATORS.*

By E. J. SCHAEFFER, M. G. PAULUS, and HARRY C. JONES.

(Concluded from p. 255).

THE concentrations of the mother-solutions used in the preparation of the solutions for the following series of measurements were the same as those employed for Table XI. The results are recorded in Tables XV. and XVI.

TABLE XV.

(I/I_0 for depth of solution = 20 mm. Temperature = 20°).

- Solution I. 75 cc. phenolphthalein, 0.5 cc. NH_4OH , 0.5 cc. NH_4Cl , diluted to 100 cc.
" II. 75 cc. phenolphthalein, 0.5 cc. NH_4OH , 1 cc. NH_4Cl , diluted to 100 cc.
" III. 75 cc. phenolphthalein, 0.5 cc. NH_4OH , 2 cc. NH_4Cl , diluted to 100 cc.
" IV. 75 cc. phenolphthalein, 0.8 cc. $N NaOH$, diluted to 100 cc.

$\lambda = A.U.$	I.	II.	III.	IV.
5773	63.2	76.2	87.3	9.9
5798	65.8	80.3	89.2	14.7
5823	72.0	82.8	91.5	20.4
5848	74.3	—	—	27.4
5948	88.8	93.3	—	57.6

The concentration of phenolphthalein is not a factor in the variations of the constants in the different tables. The following shows that it is possible to determine K_i without knowing the concentration of the indicator.

If we consider Equation 21—

$$\frac{LH \times OH}{Q} = \frac{K_w}{K_i}$$

and represent the total concentration of phenolphthalein by T , and that of the quinoid salt by Q , we have from Equation 24—

$$\frac{\ln(I/I_0) \times T}{\ln(I/I_0)'} = Q.$$

LH is then equal to $(T - Q)$ or,—

$$LH = (T - Q) = T - \frac{\ln(I/I_0) \times T}{\ln(I/I_0)'} \quad \dots (27).$$

* From the *Journal of the American Chemical Society*, xxxvii. No. 4.

TABLE XVI.

Solu- tion.	$\lambda =$ A.U.	Lactoid form. $\epsilon \times 10^3$.	Quinoid salt. $\epsilon \times 10^3$.	$\text{OH} \times 10^3$,	K_w/K_i $\times 10^3$.	$K_i \times 10^{10}$.
I.	5773	4.026	0.99	2.519	10.16	0.80
	5798	3.935	1.09	2.519	9.07	0.99
	5823	3.985	1.04	2.519	9.65	0.83
	5848	3.875	1.15	2.519	8.47	0.97
	5948	3.955	1.07	2.519	9.28	0.87
Average						0.89
II.	5773	4.43	0.59	1.26	9.46	0.86
	5798	4.45	0.57	1.26	9.77	0.83
	5823	4.42	0.60	1.26	9.24	0.88
	5948	4.39	0.62	1.26	8.82	0.92
Average						0.87
III.	5773	4.73	0.30	0.63	10.07	0.81
	5798	4.73	0.30	0.63	10.00	0.81
	5823	4.74	0.28	0.63	10.65	0.75
Average						0.79

Substituting these values in the hydrolysis equation, we have—

$$\left[T - \frac{\ln(I/I_0) \times T}{\ln(I/I_0)'} \right] \times \text{OH} = \frac{K_w}{K_i} \quad (28).$$

Simplifying, T (the concentration of the phenolphthalein) disappears, and we have—

$$\frac{\text{OH} [\ln(I/I_0)' - \ln(I/I_0)]}{\ln(I/I_0)} = \frac{K_w}{K_i} \quad (29).$$

K_i , calculated from Equation 29, gives the same value as when calculated from the equations previously derived.

Since it is not necessary to know the concentration of the indicator to determine its ionisation constant, the variation of K_i , shown by the different tables, must be due to other causes. It will be noticed from the separate tables that K_i decreases with the hydroxyl ion concentration. This is in accordance with the results of previous investigators. When the hydroxyl ion concentration, or the ratio of ammonium chloride to ammonium hydroxide, remains the same, K_i shows a marked decrease with decreasing amounts of neutral salts. If we consider Solutions III. and I. in Tables XII. and XVI., respectively, it will be seen that decreasing the concentration of the neutral salt four times, changes K_i from 1.6×10^{-10} to 0.9×10^{-10} . This is in accord with the results of Rosenstein (*loc. cit.*), who has made a very careful study of the effect of neutral salts on the ionisation constant of phenolphthalein. It will therefore be seen that the discrepancies in the value of K_i are due in part at least to the effect of the neutral salt. From this it might be concluded that K_i would be largest for those solutions containing the greatest amount of neutral salt. A study of the separate tables, Table XII. for instance, shows that just the reverse is true. The solution which contains the largest amount of neutral salt always gives the smallest concentration of hydroxyl ions, and the K_i value for such a solution is much lower than for a solution containing less neutral salt but a greater concentration of hydroxyl ions. It is thus evident that K_i varies not only with the concentration of the neutral salt but also with the concentration of the hydroxyl ions. From the above it will be seen that if the neutral salt had no effect, the variation of K_i in the separate tables would be much greater than it actually is. It is therefore obvious that the equilibrium

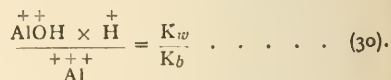
equations, based on the assumption that phenolphthalein acts as a monobasic acid, do not hold.

Wegscheider (*loc. cit.*) concludes that these variations may be accounted for by regarding phenolphthalein as a dibasic acid. The results of Rosenstein (*loc. cit.*) make it appear very probable that this indicator does act as a dibasic acid. The limitations of his method and the presence of neutral salts made it impossible for him to determine satisfactorily the ionisation constant for phenolphthalein, and the question must therefore be regarded as still open.

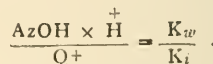
The radiometric method has thus far been applied for determining the hydrolysis and ionisation constants of indicators. Knowing these values, it is possible, by radiometric means, to determine from them the hydrolysis constants of many salts. The calculation of the ionisation constants of weak acids and bases formed by the hydrolysis of these salts is then a simple matter.

This method has been applied in a preliminary way to aluminium sulphate, using methyl-orange as the indicator. It is assumed that the secondary and tertiary hydrolysis of this salt can be neglected, and, on this assumption, the ionisation constant of the base formed by the primary hydrolysis has been calculated.

The calculations of the constants are based on two fundamental equilibrium equations, the symbols representing grm.-ions per litre. Expressing the equilibrium relation for the primary hydrolysis of aluminium sulphate we have:—



In the hydrolysis equation for methyl-orange,—



K_i has been determined and K_w is known. The concentration of the quinoid ions Q^+ is given by—

$$\text{Q}^+ = \frac{T [\ln(I/I_0) - \ln(I/I_0)']}{\ln(I/I_0)' - \ln(I/I_0)} \quad (31),$$

as explained in Equation 19. If the total amount of indicator is T, $\text{AzOH} = T - \text{Q}^+$. We then have all the data necessary for the calculation of the hydrogen ion concentration in Equation 30. The concentration of the ion AlOH^+ in the same equation is given by $\text{H}^+ + \text{Q}^+$, both of which have been determined. If T' represents the total salt added and α its dissociation, Al is $(T' - \text{AlOH})\alpha$.

The following solutions were prepared from mother solutions of methyl-orange and aluminium sulphate, the concentrations being 1.9865×10^{-4} and 0.391 grm.-molecule per litre, respectively.

- Solution 1. 50 cc. methyl orange diluted to 100 cc.
 „ II. 50 cc. methyl-orange, 5 cc. $\text{Al}_2(\text{SO}_4)_3$, diluted to 100 cc.
 „ III. 50 cc. methyl-orange, 7 cc. $\text{Al}_2(\text{SO}_4)_3$, diluted to 100 cc.
 „ IV. 50 cc. methyl-orange, 10 cc. $\text{Al}_2(\text{SO}_4)_3$, diluted to 100 cc.
 „ V. 50 cc. methyl-orange, 0.5 cc. concentrated H_2SO_4 , diluted to 100 cc.

The percentage transmissions given by these solutions are recorded in Table XVII.

The constants calculated from these percentage transmissions are given in Table XVIII. It has been found (Carnegie Institution of Washington, 1912, 'Publication No. 170, p. 60) that the dissociation of the aluminium

sulphate in Solutions II., III., and IV. is approximately 35, 52, and 30 per cent, respectively.

TABLE XVII.

(I/I_0 for depth of solution = 20 mm.).

$\lambda = A.U.$	I.	II.	III.	IV.	V.
5698	87.7	47.7	44.7	39.7	16.0
5723	88.9	56.7	53.1	—	20.1
5748	90.3	63.0	59.1	56.7	31.0
5773	91.6	70.2	66.8	63.6	39.9
5797	93.3	74.7	73.6	68.6	48.4
5823	94.5	78.4	78.1	75.5	55.1
5847	95.6	81.6	—	78.5	62.2

TABLE XVIII.

Solution.	$\lambda = A.U.$	Averages.					
		$\frac{+Q}{10^2}$	$\frac{+H}{10^2}$	$\frac{++}{10^2}$	$\frac{+++}{10^2}$	$\frac{Al}{K_w} \times 10^2$	$\frac{K_b}{K_b} \times 10^2$
II.	5698	3.56					
	5723	3.01					
	5748	3.35					
	5773	3.20					
	5797	3.37					
	5823	3.44					
	5847	3.65	6.56	1.97	2.307	6.76	6.75 1.2
III.	5698	3.94					
	5723	3.44					
	5748	3.94					
	5773	3.79					
	5797	3.50					
	5823	3.51	6.24	2.24	2.609	8.66	6.75 1.2
IV.	5698	4.62					
	5748	4.33					
	5773	4.36					
	5797	4.66					
	5823	4.16					
	5847	4.54	5.49	3.12	3.564	11.62	9.70 0.84

Summary.

A satisfactory radio-micrometer, having a half-period of ten seconds and a sensibility of 5 per square mm. of exposed vane (candle and scale being at a metre's distance) was constructed.

Making use of the radio-micrometer and the grating spectroscope, a radiometric method was worked out for the determination of the ionisation constants of indicators. This method is freer from objections and limitations than any method previously used. It serves as well for a two-coloured indicator as for a one-coloured indicator.

Very small concentrations of coloured components were determined, and it has been shown that minute concentrations of hydrogen and hydroxyl ions can be quickly and accurately estimated by means of radiometric measurements.

Satisfactory constants were obtained for the ionisation of methyl-orange as a base. The value found is 2.1×10^{-11} .

The ionisation and hydrolysis constants for phenolphthalein considered as a monobasic acid are far from being satisfactory.

From the known ionisation constant of methyl-orange and from radiometric measurements, the ionisation constant of a very weak base and the hydrolysis constant of one of its salts have been roughly determined. The method can likewise be applied for the determination of the ionisation constants of very weak acids, and the hydrolysis constants of the salts formed by these acids. Work is now in progress in the laboratory of the Johns Hopkins University on other indicators, from this same standpoint, and the results will be published in the *Journal of the American Chemical Society*.

THE TOWER SYSTEMS OF MAKING SULPHITE ACID.*

(Concluded from p. 257).

The Analysis of the Acid.

THE analysis of the acid is best done by titration with N/10 iodine solution and N/10 caustic soda solution. 1 cc. of the acid is diluted, starch solution added and titrated with the iodine until a permanent blue colour is obtained. The blue colour is then destroyed by means of a few drops of sodium thiosulphate solution. A few drops of phenolphthalein solution are added, and caustic soda run in until a red colour is obtained. The number of cc. of iodine solution added indicates the total amount of SO_2 present, and the difference between double the quantity of iodine solution and the quantity of caustic soda solution used indicates the amount of combined SO_2 .

Multiplying by 0.32 gives the percentage of free and combined SO_2 in the acid. The percentage of lime (CaO) in the acid is to the combined SO_2 as 28 to 32. This test does not give an absolutely correct result, due to the fact that some of the SO_2 evaporates during the test and to other reasons, but made with care this test will give a result accurate enough for all practical purposes.

Capacity of Acid Plant.

It is difficult to give absolute figures for the capacity of the different machines and apparatus in an acid plant, but the accompanying are approximate figures calculated in tons of pulp per day.

The ordinary retort burner is sufficient for two and a-half to five tons production.

Rotary burners are built for all productions up to forty tons. The standard Herreshoffs pyrite burner is sufficient for twelve and a-half tons.

The capacity of gas coolers has already been mentioned.

Each tank in a high tower system gives acid for twelve fifteen tons, and low towers in series about the same.

Chamber systems are built for up to thirty tons.

Milk of lime systems are built for all productions up to 100 tons.

Digesters and the Cooking.

There are two different methods of cooking, heating by indirect steam and cooking with direct steam. In some mills these systems are combined.

Mitscherlich (extra strong, as well as bleachable) and ordinary strong pulp, is cooked with indirect heating, sometimes in connection with direct steam; ordinary bleachable and "quick cooked" pulp is invariably cooked with direct steam.

The digesters are of varying size and construction. In old mills there are still in use digesters with a capacity of two tons or even less, lying stationary, as well as rotary supported on rollers or on bearings. The most commonly used digester is, however, the standing stationary type of five to fifteen tons capacity.

The best type of this digester is one with the diameter about one-third of the total length, the lower end consisting of a cone of about 60° , ending in a blowout pipe, and the upper end consisting of a cone of about 110° , ending in a good-sized manhole. This latter design enables the digester to be well filled with chips in a short time, and without too much work.

Digesters are now without exception lined with single or double layers of acid-proof bricks set in acid-proof mortar, with or without a sheet lead jacket behind. Usually the bricks are three and two inches thick, respectively; in some cases bricks as thin as one and a quarter inch are used, in order to save space, but they are just as expensive as thicker bricks, and do not stand wear and tear as well.

* *Chemical Engineer*, xxi, No. 6. (Reprinted from *Paper*).

Only non-porous bricks should be used, and they should be set half an inch apart, to make it easy to clean the joints of mortar affected by the acid, and replace it. Well pressed and burnt red bricks are nowadays extensively used for digester lining, but tests should be made before a new brand of these bricks are used, as bricks apparently non-porous may turn out to be porous when used.

Acid-proof mortar is usually composed of one part of Portland cement to one or two parts of crushed and sifted acid-proof brick, often in combination with litharge and asbestos. In order to make the mortar harden quickly, it is made with a 4° Bé. solution of silicate of soda, instead of water, and this silicate of soda is during the first cook transformed into an acid-proof compound. Care should be taken that no part of the mortar hardens before it is put in position in the lining, as it is liable to break up when applied and form weak spots in the lining.

Where the digester shells are not absolutely tight, one should line the digester first with a jacket of thin sheet lead, perfectly tight, because the acid is liable to work its way through the mortar to every leak. The lead lining, however, has its weak points, as it creeps and buckles from the effect of the difference in temperature and separates the lining from the shell, which must be perfectly smooth inside, in order not to wear the lead out too quickly.

The best way to get a good reliable lining is to see that the digester shell is perfectly tight, at a hydraulic pressure one and a half times as high as the working pressure. The shell is next lined with a one inch layer of mortar which is not brittle—i.e., acid-proof mortar mixed with a considerable amount of asbestos, or fat lime, or both. On this is laid one layer of three inches, or two layers of thinner acid-proof brick.

The joints of the last layer of bricks can be filled in to the depth of about half an inch with a mortar made of litharge and specially prepared glycerin. This mortar resists the acid well but is brittle, and should be examined from time to time and renewed if cracked, in order to prevent the acid from attacking the mortar underneath.

The lining should, at the manholes and pipes, end up against disks, or pipes made of hard acid-proof metal, cleaned but rough, but should not end up against lead. Where lead lining is used the main body of the shell is covered with about one quarter of an inch of sheet lead and half an inch lead at all pipe inlets and manholes.

Miscellaneous Fittings.

The necessary fittings are two inlet pipes for steam, at or near the bottom of the digester, blow-off valve right at the bottom, or a manhole where the pulp is discharged by gravity, two outlet pipes for gas at the top of the digester, steam pressure gauge, thermometer pocket, and sample cocks. Sometimes digesters are arranged with only one pipe outlet at the top of the digester, combined with an acid proof pipe with valve connections to acid pipe, blow-off gas pipes, steam gauge, &c.

In indirect cooking five to eight inlet holes for steam are arranged at or near the middle of the digester, and as many at or near the bottom, each hole provided with a valve and check valve respectively, at inlet and outlet. The inlet and outlet holes are connected inside the digester by means of copper pipes, laid spirally round the digester and supported by acid-proof racks.

The blow-off valve should be of ample size, not less than eight inches, connected to an acid-proof bend on the bottom of the digester. Where there is water available of a higher pressure than the blow-off pressure a water connection should be fitted to this bend, so arranged that the water goes in the same direction as the pulp, but it must be taken into consideration that this cold water gets available so as to adhere to the fibres, and this scheme should therefore not be used where there is a large proportion of rosin in the wood.

Steam can also be used to quicken the blowing off and is arranged in the same way as mentioned for water. The blow-off valve should be so constructed that it gives as little resistance as possible to the pulp.

The pipes from the digesters to blow pits can be made either of thin copper or cast-iron. The pitch in the blown off liquor will corrode the cast-iron pipes and prevent the SO₂ gas left in the liquor from affecting the pipe. Pipes from acid storage tanks to digesters should be made of copper or hard lead, pipes from digesters to coolers should be made of extra hard lead (3 per cent antimony), or even better of copper, which, however, is more expensive. The fittings on the digesters should be made of best quality phosphor-bronze, other acid-proof fittings can be made of cheaper materials.

In older mills where scrap metal is available, and where a considerable crew has to be kept for the Sunday repairs—a crew which it is often hard to find work for during the week-days—it will pay to make these fittings. All kinds of scrap metal, old brass, bearings, valves, &c., are melted in a graphite crucible, and the zinc well "burnt off." To every 6 lbs. of this burnt-off metal add 10 lbs. of phosphorous tin and 30 to 35 lbs. of scrap lead. Cast at as low a temperature as possible and stir well in the crucible before and during the casting, preferably with well dried hardwood branches with the bark left intact, in order to get the oxides of the metals to the surface.

This metal resists the acid well, and can be used in casting pumps, valves, &c., but should not be used for digester fittings.

Gaspipes from the digesters to the coolers and acid storage tanks should be three to four inches in diameter, depending on the size of the digesters. In case screens are arranged inside the digesters to prevent chips and pulp from plugging the gas pipes, these should be made so that no chips can collect on or near them, as these chips will be burned by the steam during the cooking, and form black specks in the pulp which cannot be bleached.

POTASH FROM FELSPAR.

THE cost in Germany of producing one unit of potash (20 lbs. of K₂O) in the form of commercial "muriate" is known to be less than 15 cents; adding all handling and sales costs and a reasonable return upon the money in use the cost per unit ex-ship U.S. Atlantic seaboard does not exceed 30 cents. Hence, if at the close of the present European war Germany still remains a member of the family of nations and plies its foreign trade as heretofore, no potash mine, method, or process having a producing cost of 30 cents or more per unit can possibly survive German competition.

Felspar deposits of vast extent have been located, having an average run-of-mine composition as follows:—

K ₂ O	..	..	..	..	..	..	..	11	per cent
Na ₂ O	..	..	..	..	..	..	..	2	"
SiO ₂	..	..	..	..	..	..	..	70	"
Al ₂ O ₃	..	..	..	..	..	..	..	17	"

The soda has no value, as the cost of separating soda from potash would probably exceed the market worth of the recovered soda. Assuming potash worth f.o.b. factory 29 cents per unit, and alumina, 100 per cent pure and free of iron and silica, three-fourths of a cent per pound, and the silica 25 cents per short ton; the total values in one short ton of felspar aggregate 5 dols. 92 cents. It is true that alumina of the purity indicated cannot be purchased at this time for less than 3 cents per pound, but that price is the result of something of the nature of a "gentleman's agreement." Alumina produced in any quantity must to find a market displace bauxite, and must be prepared to meet bauxite prices.

The bald facts seem to imply that no felspar potash re-

covery process is worthy of investment support unless it is able to operate at a cost of 5 dols. 92 cents per short ton of felspar, including upkeep, and an attractive return on the investment involved.

There are very many felspar recovery processes, and prominent among them are those using spar as a substitute for clay in making Portland cement. This general project has much in its favour, because of the unlimited market for the cement by-product. However, under average conditions the cost of materials, clay and lime, in Portland cement making amounts to less than 3 cents per 100 lbs.; hence, for making such cement one short ton of felspar has an apparent value of:—

11 units of potash at 29 cents .. 3 dols. 19 c. per lb.
17.4 cwt. silica, &c., at 3 cents. 52 c. "

3 dols. 71 c. "

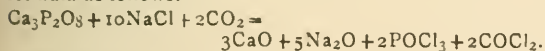
Against this must be charged the cost of the spar and process for extracting the potash and a reasonable profit on the capital invested in the potash recovery process. The values are discouragingly low for the purpose.

It seems evident that a commercially successful felspar process must not only effect the recovery of the potash, but in doing so must create other industrial values. To illustrate: a mixture of felspar and potassium chloride heated to 1050° C. produces potassium silicate and aluminium chloride, which latter is of course removed in process by sublimation. The potassium silicate is easily and cheaply converted to potassium carbonate and a pure iron-free silica. The aluminium chloride may be easily converted to alumina and carbon oxychloride, which reacts with felspar to make potassium chloride, &c.; that is, the chlorine may become largely cyclic. This process, while vastly more hopeful than the cement or alkali extraction processes for decomposing felspar, still verges sharply on the limit of cost and provides a margin of safety too narrow to justify investment capital.

There remains possible the utilisation of felspar as a decomposition phase in producing commercial soda-ash, or caustic, and this method has been carefully examined by trained investigation. The results are given in brief in the following description.

Felspar—Soda Ash Process.

A mixture of phosphate rock and common salt is heated to 1100° C. in a muffle furnace, in which an inert gas such as carbon dioxide is slowly flushed through the furnace chamber. The phosphorus and chlorine are removed by volatilisation, leaving the soda and lime as furnace residue. The reaction may be stated in proportional formula as follows:—



This reaction is governed by no time factor other than fuel economy, hence the operation may be continued at will and a very high reaction efficiency realised.

From the furnace residue the soda is extracted by leaching, and is marketed either as caustic or as soda-ash, for which purpose the waste fuel gases are utilised; the furnace fuel is producer gas. This is the first step, and a low cost sodium salt is changed to forms in which its industrial value is tripled.

The second step consists in passing the phosphorus and carbon oxychlorides over felspar heated to 600° C. in a muffle furnace. By this treatment the potash and alumina in the felspar are converted to chlorides and the alumina chloride is volatilised and passes out of the furnace. The furnace residue consists of silica and potassium chloride, and the latter is extracted by leaching, and is converted to the commercial "muriate" by utilisation of waste furnace gases. The phosphorus, of course, becomes P_2O_5 .

The volatilised aluminium chloride is separated from any iron chlorides present by simple fractionation, and is then volatilised in the presence of carbon dioxide or

sulphur dioxide, through a baffled furnace chamber heated to 800° C. (about the dissociation temperature of carbon oxychloride), and alumina and carbon oxychloride are formed, thus: $2\text{AlCl}_3 + 3\text{CO}_2 = \text{Al}_2\text{O}_3 + 3\text{COCl}_2$, and the carbon oxychloride is returned to process. As a final product all of the potash becomes chloride, and the alumina of the spar is separated as such, and free of silica, alkali, or iron.

Assuming a plant decomposing 40 short tons of tricalcium phosphate per day, the materials required, assuming both phosphate and felspar are used in 5 per cent excess, are as follows:—

Phosphate rock, 70 per cent. .. 53 long tons
Common salt 76 short tons
Felspar 455 short tons

The daily products would be:—

Phosphoric oxide, 100 per cent .. 36,570 lbs.
Soda-ash, 97 per cent 133,910 "
Potash chloride, 50 per cent K_2O 190,646 "
Alumina, 100 per cent 147,000 "

The furnace fuel may be closely approximated by adding to the thermochemical heat summation of each reaction the sensible heat in the reaction products at the reaction temperature. For all the reactions involved, assuming a fuel coal of 3000 kilogram.-calories value per pound and an efficiency of 15 per cent for the high temperature furnaces and 20 per cent for those of low temperature, the total fuel required per day amounts to 178 long tons.

Plant and operation data are approximately as follows:—

The high temperature furnaces treat daily 130 tons of charge, and assuming fairly large furnaces, with two always in reserve, twelve will be required. The cost of this equipment emplaced should not exceed 90,000 dols. and the daily operating labour should not exceed 60 dols. The low temperature furnaces treat daily 460 tons of charge, of which about 80 tons are given a second treatment. About sixteen furnaces will be required, involving a plant outlay of about 75,000 dols. and a daily operating labour charge of about 30 dols.

The gas producers burn 180 tons of coal per day and will cost about 40,000 dols., with a daily operating labour charge of 20 dols. The soda-ash plant will cost 40,000 dols., with a daily operating labour charge of 20 dols.

The power and milling plant will cost about 50,000 dols., with a daily operating labour charge of 25 dols. There should be ample waste heat to generate all the steam required.

Buildings and land, with total miscellaneous equipment, including office and laboratory with fittings, will cost about 80,000 dols. The daily miscellaneous labour charge, covering incidental work, &c., will not exceed 50 dols.

The daily management and supervision may be approximated as follows:—Superintendent, with two assistants, 26 dols.; chemist and assistant, 9 dols.; three mechanics, 12 dols.; clerical services, 10 dols.; total, 57 dols.

The total plant cost should not exceed 375,000 dols., and the daily pay-roll 262 dols.

The annual general charges should not exceed:—

Plant depreciation at an average of
10 per cent. 37,500 dols.
Insurance, taxes, &c. 12,000 "
Supplies and office expenses 45,000 "
Executive and legal 10,000 "
Interest on stocks at 5 per cent. .. 15,000 "

Total 119,500 "

The plant is assumed to have a producing year of 340 days, but an operating year of 360 days; that is, 20 days of each year are devoted to repairs and the training of men and machinery.

To the operating cost must also be added a certain proportion of about 50,000 dols. to cover the usual cost of start-

ing a new plant, training men, and balancing machinery. This charge is properly an operating expense, and is distinguished with its interest charge by even payments extending over a period of about six years; hence, to the annual operating costs for the first six years must be added about 10,000 dols. yearly.

The following general summary of annual costs may be characterised as conservative:—

Phosphate, 18,020 long tons at 5 dols.	90,100 dols.
Salt, 26,180 short tons at 5 dols.	130,900 "
Felspar, 154,700 short tons at 1 dol.	154,700 "
Coal, 60,520 long tons at 3 dols. 50c.	211,820 "
Pay-roll	94,320 "
New plant expenses	10,000 "
General accounts	119,500 "
Total	811,340 "

Assuming a producing year of 340 days, the annual value of products should be as follows:—

Phosphoric oxide, 100 per cent, 6208 tons at 40 dols.	248,320 dols.
Soda-ash, 97 p.c., 22,763 tons at 10 dols.	227,630 "
Alumina, 100 p.c., 24,990 tons at 15 dols.	374,850 "
Total	850,800 "

Exclusive of the potash, this process indicates a profit of 39,460 dols. yearly, which should amply cover all process rights, &c.

The potash produced per year amounts to 32,300 short tons of "muriate" of a grade corresponding to 50 per cent K_2O , and so far as factory costs are concerned may be written off as produced free of cost.

Phosphoric oxide (P_2O_5) is valued at 40 cents per unit, and this requires explanation. This product would be recovered as phosphoric acid (H_3PO_4) of any desired concentration, and would be used to replace sulphuric acid in converting gaseous ammonia at by-product coke plants, &c., to solid form. The cost of sulphuric acid combined with one unit of ammonia as ammonium sulphate ranges from 30 to 50 cents, depending on the delivered cost of sulphuric acid, and, as in ammonium phosphate, this sulphuric acid would be replaced by a trifle more than two units of P_2O_5 ; evidently the acid value of P_2O_5 is about 15 cents per unit, minimum. Deducting this from the 40 cents per unit estimated value leaves a fertiliser value of 25 cents per unit of P_2O_5 , a value markedly lower than any other source of water soluble phosphoric acid known at this time.

The limiting factor of this process is the consumption of alumina. For every unit of potassium oxide recovered about 30 lbs. of alumina are produced. However, an independent source of iron and silica-free alumina at so low a cost as 15 dols. per short ton would no doubt enable the price of metal aluminium to be cut in half, and thereby vastly extend the consumption of that metal. To do this it would possibly be necessary to foster aluminium-producing industries other than those now in operation, probably not a very difficult undertaking if suitable alumina at 15 dols. per ton is guaranteed. — *Chemical Engineer*, xxi., No. 5.

X-Rays and Metals.—Nobel Prizeman to Give May Lecture.—The awarding of the Nobel Prize for Physics for 1915 by the Swedish Royal Academy of Science to Prof. W. H. Bragg, M.A., D.Sc., F.R.S., of University College, Gower Street (jointly with his son), for an examination of the formation of crystals by X-rays, renders of special interest the announcement that Prof. Bragg is to deliver the 1916 May Lecture before the Institute of Metals. The May Lecturer is now devoting attention to the structure of metal crystals as revealed by X-rays, and it is expected that he will have a very important pronouncement to make on this subject before the Institute of Metals on the occasion of the forthcoming Lecture.

THE DETERMINATION OF NITRIC NITROGEN IN SOILS.*

By E. R. ALLEN.

(Continued from p. 252).

Experimental.

Choice of Indicator for the Titration of Ammonia.

SINCE a reduction method for nitric nitrogen involves the titrimetric determination of ammonia, an indicator suitable for the titration of weak bases had to be chosen. Preliminary tests convinced us that methyl red, *p*-dimethyl-amino-azo-benzene-*o*-carboxylic acid (Note 2), is easily the best indicator that has yet appeared for the titration of weak bases as ammonia. It is possible to titrate with ease N/50 solutions of ammonia against strong acids, provided no CO_2 is present. We have observed also that the end-point is more distinct if the solution to be titrated is cooled to 10–15° C. This is doubtless due to cutting down of hydrolysis of the ammonia salt of the complex organic acid indicator at this temperature. The end-point is more certain than with either Congo red or alizarin red, and vastly more distinct than with methyl orange, lacmoid, or cochineal. Another advantage is that its colour change takes place at a lower concentration of hydrogen as ion than does that of methyl orange. According to Tizard (*Journ. Chem. Soc. Trans.*, 1910, xcvi., 2477) the visible colour-change, red to yellow, takes place between 10–57 and 10–7, while A. A. Noyes (*Journ. Am. Chem. Soc.*, 1910, xxxii., 824) reports that the transition colour of methyl red is most marked at $(H^+) = 10^{-6}$ as compared with $(H^+) = 10^{-4}$ for methyl orange. Throughout this work we have adhered to the first faint appearance of brown—free from pink—in the pale lemon-yellow alkaline solution as our end-point.

Preparation of Materials and Solutions: Titrimetric Standards.—Tenth and fiftieth normal solutions of sulphuric acid and of sodium hydroxide were prepared free from CO_2 , and were standardised by the sodium carbonate method which Mitscherlich and Meeres (*Land. Jahrbücher*, 1910, xxxix., 345) found the most accurate. 50 cc. burettes (Note 3), provided with three-way stop-cocks, connected with the reservoir bottle, essentially as recommended by Treadwell, were used ("Analytical Chemistry," 1910, ii., 3d ed., 556). The white-topped titrating shelf was directly in front of a south window, and the entering light was diffused by passage through a sheet of white paper. The method of reading the burettes was that specified by the Bureau of Standards (*loc. cit.*, 17). When portions of the solutions had stood in the burettes twenty-four hours or more they were discarded. Temperature corrections were made when necessary.

Analytical Standards.—The sources of nitric and ammonia nitrogen used in the testing of methods reported in this paper were solutions of nitric acid and of ammonium hydroxide. These were prepared from carefully neutralised (Note 4) ammonia-free water and C. P. HNO_3 or NH_4OH . They were accurately standardised against the titrimetric standards by series of titrations.

Ammonia-free Water.—The regular laboratory-distilled water was treated with bromine water till the tint was distinctly yellowish, allowed to stand at least four hours, transferred to a 5-litre Jena balloon flask, sufficient alkali added to destroy the colour, distilled through an ordinary glass condenser, and stored in glass-stoppered bottles. Of course water so prepared reacted slightly alkaline. Whenever used in titrimetric operations it was carefully neutralised beforehand with N/50 H_2SO_4 . When CO_2 -free water was desired the receiver was protected with a soda-lime tube. This water was used in all operations reported in this paper.

* From the *Journal of Industrial and Engineering Chemistry*, vii., No. 6.

Ammonia-free Magnesias.—J. T. Baker's C. P. Magnesium oxide was heated in an electric furnace one hour or more at a temperature of 700 to 800° C.

Soil Extracts High in Organic Matter but free from Nitric Nitrogen.—1 kilogram. of air-dried greenhouse soil, which had been heavily manured for several years and had recently received a liberal application of barnyard manure, was well shaken with two litres of water containing 20 grms. of dextrose and allowed to stand over night. It then showed not the slightest trace of nitrate by the diphenylamine test. 350 cc. gave on distillation with magnesium oxide 0.32 and 0.37 mgrm. of ammonium nitrogen, and after Kjeldahl digestion 2.27 mgrms. of organic nitrogen.

The solution was very highly coloured, appearing decidedly reddish in the deeper layers. It represents an extreme though not an impossible case. Its reducing power was tested by titration with Fehling's solution. 10 cc. portions of the extract reduced 8.60, 8.48, and 8.56 cc. of Fehling's solution.

Aluminium-Copper-Zinc Alloy.—The regular Devarda alloy (Cu 50 : Al 45 : Zn 5) was used and not that recommended by Valmar. The Devarda alloy is purchasable on the market and met the requirements of our work. J. T. Baker's product was used, which was found to be absolutely free from nitrogen. A product purchased from another dealer contained, oddly enough, an appreciable amount of nitrogen. The J. T. Baker product was obtained in the form of a powder, much of which would not pass a 20-mesh sieve. Before use it was all pulverised to pass a 60-mesh sieve.

Diphenylamine Reagent.—In an investigation of this sort it is of course necessary to have a means of determining qualitatively minute amounts of nitric nitrogen. The diphenylamine-sulphuric acid method as modified by Withers and Ray (*Journ. Am. Chem. Soc.*, 1911, xxxiii., 708) meets this requirement. We followed their directions except that as a rule the solutions were tested at room temperature instead of at 40°. By actual tests the reagent we used gave under these conditions a faint but distinct reaction in a solution containing 1 part of nitric nitrogen in 25,000,000. The responses to this reaction are classified in the accompanying tables as strong, faint, and none.

Indicator Solution.—Two-hundredths of a gm. (0.02) of methyl red i.e., the free acid—were dissolved in 100 cc. redistilled alcohol (Note 5). Four drops of this solution were used per titration.

Choice of Reduction Procedure.—Three methods were tested for their applicability to our conditions:—

1. **The Aluminum Reduction Method.**—The procedure that was employed by Burgess (University of California Publications in Agri. Sci., 1913, i., No. 4) except that one-half the amount of soil extract, containing only 12.5 mgrms. nitric nitrogen, was used. The soil extracts, $\times 25$ cc. N_2O_5 and 2 cc. of 50 per cent NaOH, were concentrated to about 40 cc. by gentle boiling. The volume of the reducing solutions was 60–70 cc. It was observed that the action on the aluminum was much slower in the presence of organic matter than in the checks. In the latter the aluminum strips completely dissolved over night, while in the former they had been but slightly attacked and were coated with a thin gelatinous layer of organic matter. In obtaining the data of Table I. these strips were left in the flask during distillation in Nos. 2c and d and 3c and d, while in the cases of Nos. 2a and b, 3a and b, and all of Set 4, they were washed off and discarded.

It is believed that the production of ammonia from organic matter entered somewhat into the determinations of Set 4. This action would, of course, be greater in the longer reduction periods. This would explain why No. 4a gave high values for nitrate and still by the diphenylamine method showed considerable nitrate unreduced.

TABLE I.—*Recovery of 12.5 Mgrms. of Nitric Nitrogen by the Aluminum Reduction Method.*

Set No.	Material.	No. hours reduction.	Mgrms. N found.	PH ₂ NH reaction. (a)
1.	Check	16 at 20-22° C.	<i>a</i> 12.26 <i>b</i> 12.29 <i>c</i> 11.95 <i>d</i> 12.34	Faint None " Faint
2.	Soil extract ..	16 at 20-22° C.	<i>a</i> 8.11 <i>b</i> 8.25 <i>c</i> 10.60 <i>d</i> 7.50	} Strong
3.	Do., clarified with lime	} 16 at 20-22° C.	<i>a</i> 3.81 <i>b</i> 4.82 <i>c</i> 5.91 <i>d</i> 8.10	
4.	Ditto		40 at 20-22° C.	<i>a</i> 12.60 <i>b</i> 12.15 <i>c</i> 10.16 <i>d</i> 12.38

(a) The diphenylamine reactions reported in this and subsequent tables are the results of tests made on 1 cc. portions of the solutions after reduction.

The data in Table I. indicate that the claims made for this method by Burgess are too broad. Organic matter evidently *does* retard the reduction. It should be noted here also that the aluminum reduction method has been prescribed for the determination of nitric nitrogen in waters "if the quantity of organic nitrogen is less than 0.1 part in 100,000" (Sutton's "Volumetric Analysis," 1911, 10th ed., 465). The organic materials used by Burgess—i.e., soluble humus and dextrose—do not contain the type of colloidal matter that is encountered in extraction of soils containing decaying organic matter. Furthermore, it is doubtful if a method which involves the transfer of a solution containing ammonia in the presence of a fixed alkali will yield highly satisfactory results. At any rate the procedures described below involved less time and gave promise of greater accuracy.

(To be continued).

INTERNATIONAL ATOMIC WEIGHTS.

1916.

	Symbol.	Atomic weight.
Aluminium	Al	27.1
Antimony	Sb	120.2
Argon	A	39.88
Arsenic	As	74.96
Barium	Ba	137.37
Bismuth	Bi	208.0
Boron	B	11.0
Bromine	Br	79.92
Cadmium	Cd	112.40
Cæsium	Cs	132.81
Calcium	Ca	40.07
Carbon	C	12.005
Cerium	Ce	140.25
Chlorine	Cl	35.46
Chromium	Cr	52.0
Cobalt	Co	58.97
Columbium	Cb	93.5
Copper	Cu	63.57
Dysprosium	Dy	162.5
Erbium	Er	167.7
Europium	Eu	152.0
Fluorine	F	19.0
Gadolinium	Gd	157.3
Gallium	Ga	69.9

	Symbol.	Atomic weight.
Germanium	Ge	72.5
Glucinum	Gl	9.1
Gold	Au	197.4
Helium	He	4.00
Holmium	Ho	163.5
Hydrogen	H	1.008
Indium	In	114.8
Iodine	I	126.92
Iridium	Ir	193.1
Iron	Fe	55.84
Krypton	Kr	82.92
Lanthanum	La	139.0
Lead	Pb	207.20
Lithium	Li	6.94
Lutecium	Lu	175.0
Magnesium	Mg	24.32
Manganese	Mn	54.93
Mercury	Hg	200.6
Molybdenum	Mo	96.0
Neodymium	Nd	144.3
Neon	Ne	20.2
Nickel	Ni	58.68
Niton (radium emanation)	Nt	22.4
Nitrogen	N	14.01
Osmium	Os	190.9
Oxygen	O	16.00
Palladium	Pd	106.7
Phosphorus	P	31.04
Platinum	Pt	195.2
Potassium	K	39.10
Praseodymium	Pr	140.9
Radium	Ra	226.0
Rhodium	Rh	102.9
Rubidium	Rb	85.45
Ruthenium	Ru	101.7
Samarium	Sa	150.4
Scandium	Sc	44.1
Selenium	Se	79.2
Silicon	Si	28.3
Silver	Ag	107.88
Sodium	Na	23.00
Strontium	Sr	87.63
Sulphur	S	32.06
Tantalum	Ta	181.5
Tellurium	Te	127.5
Terbium	Tb	159.2
Thallium	Tl	204.0
Thorium	Th	232.4
Thulium	Tm	168.5
Tin	Sn	118.7
Titanium	Ti	48.1
Tungsten	W	184.0
Uranium	U	238.2
Vanadium	V	51.0
Xenon	Xe	130.2
Ytterbium (Neoytterbium)	Yb	173.5
Yttrium	Yt	88.7
Zinc	Zn	65.37
Zirconium	Zr	90.6

OBITUARY.

PROF. RAPHAEL MELDOLA, F.R.S.

THE news of the sudden death of Prof. Raphael Meldola, which occurred on November 16, at the age of sixty-six, will be received with deep regret. Prof. Meldola was actively engaged in scientific work and his powers showed no abatement or flagging; his vigorous and energetic personality gave him great influence among his wide circle of friends and pupils, and he will be much missed in the scientific world.

Meldola received his education at the Royal School of

Mines, afterwards working for two years in the colour factory of Messrs. Williams, Thomas and Dörner. In 1872 he received an appointment at the Royal College of Science, where he also acted as private assistant to Sir Edward Frankland. Afterwards he became assistant to Sir Norman Lockyer in the Solar Physics Laboratory, and in 1875 he went to the Nicobar Islands in charge of the expedition for the observation of the total eclipse of the sun. Subsequently he again obtained an appointment in dye works, and while he was with Messrs. Brooke, Simpson and Spiller he made some important discoveries in connection with the coal-tar dyes. In 1885 he was elected Professor of Chemistry at the Finsbury Technical College. He was President of the Chemical Society in 1905-7, of the Society of Dyers and Colourists in 1907-8, and of the Society of Chemical Industry in 1908-9. He was elected a Fellow of the Royal Society in 1886, and the Davy Medal was conferred upon him in 1913. Prof. Meldola was firmly convinced that the neglect of pure research in Great Britain was chiefly responsible for the decline of industry in England, and was assiduous in putting his views before the public. He was appointed a member of the Advisory Council for the Organisation and Development of Scientific and Industrial Research, where his special knowledge and sound views would have been of the greatest service. He was the author of text-books on the Chemistry of Photography and on the Synthesis of Vital Products, and also translated and edited Weissmann's "Studies in the Theory of Descent," a subject in which he was greatly interested.

MEETINGS FOR THE WEEK

MONDAY, 29th.—Royal Society of Arts, 4.30 (Cantor Lecture). "Optical Glass," by W. Rosenhain.

TUESDAY, 30th.—Royal Society. (Anniversary Meeting). President's Address.

— Royal Society of Arts, 4.30. "Recent Developments in Jamaica, Interneta and External," by Sir Sydney Olivier.

WEDNESDAY, Dec. 1st.—Royal Society of Arts, 4.30. "Insects and War," by Arthur Everett Shipley.

— Society of Public Analysts, 8. "Micro-chemistry of some Alkaloids," by G. D. Lander. "The 'Presumptive Coli Test' on Unchilled Water," by W. Partridge. "Methods of Analysing Oleaginous Seeds and Fruits," by E. R. Bolton.

THURSDAY, 2nd.—Royal Society. "Existence of Converging Sequences in certain Oscillating Successions of Functions," by W. H. Young. "Emulsifying Action of Soap—A Contribution to the Theory of Detergent Action," by S. A. Shorter and S. Ellingworth. "The Newtonian Constant of Gravitation as affected by Temperature," by P. E. Shaw. "Skin Friction of the Wind on the Earth's Surface," by G. I. Taylor.

— Chemical, 8. "Comparative Method for Determining Vapour Densities," by P. Blackman. "Isomerism of the Oximes—Part VII., 5-Bromovanillinaldoxime, 5-Nitrovanillinaldoxime, and 6-Nitropiperonaldoxime," by O. L. Brady and F. P. Dunn. "Rate of Growth of Bacteria," by A. Slator. "Study of Binary Mixtures—Part I., Densities and Viscosities of Mixtures containing Phenol," by A. Bramley. "Studies in Catalysis—Part III, Preliminary Measurements of the Infra-red Absorption Spectra of Hydrogen Chloride, Potassium Chloride, and Methyl Acetate in Aqueous Solution," by R. H. Callow, W. C. McC. Lewis, and G. Nodder; Part IV., "Stoichiometric and Catalytic Effects due to the Progressive Displacement of one Reactant by another in the 'Acid' Hydrolysis of Methyl Acetate," by R. O. Griffith. "Colorations Produced by some Organic Nitro compounds, with special reference to Teranitromethane," by A. K. Macbeth. "The Catalytic Bleaching of Palm Oil," by S. G. Sastri. "The Propagation of Flame in Mixtures of Hydrogen and Air—The 'Uniform Movement,'" by W. A. Hayward and T. Otagawa.

ERRATA.—P. 235, col. 2. "Yield of Paper on Green Stem of Banana." The headings to the table require to be transposed, thus:—"Dressed fibre on green weight of plant" should come over the first of the three columns (1.49 per cent); "Tons of green weight per ton of fibre" over second column (6.5); "Tons of green weight per ton of paper" over third and last column (132.4).

THE CHEMICAL NEWS.

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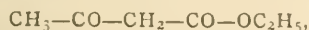
THERMO-DYNAMICAL OBJECTIONS TO THE MECHANICAL THEORY OF LIFE.

By H. STANLEY REDGROVE, B.Sc. (Lond.), F.C.S.

IN the late Professor Carl Schorlemmer's "The Rise and Development of Organic Chemistry" (revised edition, edited by A. Smithells, B.Sc., 1894, p. 266), the following passage is quoted from Kekulé:—"The hypothesis of chemical valency further leads us to the supposition that also a relatively large number of single molecules may, through polyvalent atoms, combine to *net-like*, and if we may say so, *sponge like masses* in order thus to produce those molecular groups which resist diffusion, and which, according to Graham, are called colloids. The same hypothesis leads us, in a most natural manner, to the view already pronounced by . . . Pflüger, that such a cumulation of molecules may extend yet further, and thus build up the *formative elements* of living organisms. Of these *mass-molecules* we may perhaps further suppose that, through the constant change of position of polyvalent atoms, they will show a constant change in the connected individual molecules, so that the whole—of course with development of electricity—is in a sort of living state; particularly so as, through similar displacements, adjacent molecules may be drawn into the circle of combination and newly-formed ones expelled."

The most characteristic property of life, or rather of living matter, is its spontaneous activity. In the above quotation we have an attempt to explain this spontaneous activity chemically, as due to reiterated molecular rearrangement. And since chemical action is regarded as being ultimately explicable in terms of mechanics, the hypothesis forms a useful adjunct, if not a necessary step, in the mechanical theory of life. But as formulated by Kekulé, the hypothesis is of a very vague and speculative character, and one is led to ask: Are there any bodies known in the case of which there is definite chemical evidence for believing in such reiterated molecular arrangements?

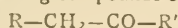
The answer involves a discussion of Laar's theory of tautomerism. There are many bodies known to chemists which behave in certain circumstances as if they possessed one molecular configuration, in other circumstances as if they possessed another molecular configuration. There are also many bodies, capable of being synthesised in more than one way, whose different syntheses lead us to regard more than one formulæ as equally probable for them. The most celebrated example of the first class is aceto-acetic ester, which, whilst usually behaving as a ketone of formula—



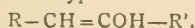
—gives a sodium salt derived from the isomeric unsaturated alcohol—



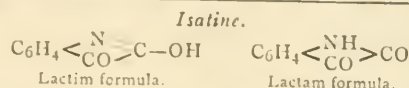
But, in fact, the phenomenon is shared by many ketones and aldehydes, which, usually reacting as true keto-bodies, *i.e.*, carbonyl-containing compounds of the type—



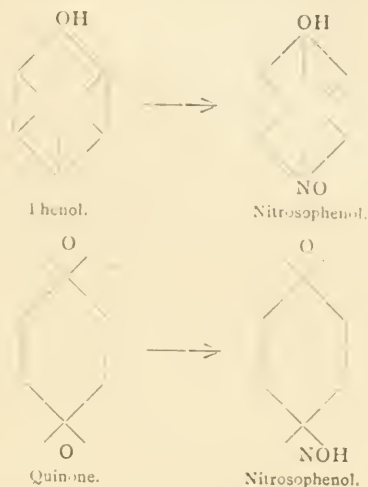
(where R, R' may be H, CH₃, C₂H₅, &c.)—also form sodium derivatives, as though they were unsaturated alcohols (enols), of the type—



Another example is afforded by isatine, which gives derivatives of two types, distinguished by the names "lactim" and "lactam," thus—



Of the second class of bodies may be mentioned nitroso-phenol, which may be made not only by the action of nitrous acid on phenol, but also by that of hydroxylamine on quinone, though these syntheses one would expect to yield different bodies, thus:—



And many more instances could be adduced.

In all these cases it will be noticed that the difference between the alternative formulæ is in the position of a hydrogen atom. Now, according to Laar, such pairs of formulæ do not represent distinct bodies, since this hydrogen atom, called "labile," is supposed continually to oscillate from one position to the other. But chemical identity is a question of energy, and we are not entitled to assume the identity of such formulæ, if it is found that they represent different quantities of energy. This point may be settled from thermochemical data, and most conveniently by considering the heats of combustion of such bodies.

Let (x) stand for the effect on heat of combustion of a grm.-atom of separated atoms of the element x, or separated molecules of the group x, and let (x.y) stand for the effect on heat of combustion caused by severing the bonds between a grm.-atom of atoms of x and a grm.-atom of atoms of y. Then, confining our attention to the case of aldehydes and ketones, we have:—

Molecular heat of combustion given by keto formula—
R—CH₂—CO—R' equals
(R) + (R') + 2(C) + 2(H) + (O) + 3(C.C) + 2(C.H) + (C.O),
and—

Molecular heat of combustion given by enol formula—
R—CH=COH—R' equals
(R) + (R') + 2(C) + 2(H) + (O) + 2(C.C) +
+ (C.C) + (C.H) + (C.O) + (O.H).

Now let—

$$\theta = (R) + (R') + 2(H) + 2(C.H).$$

$$\alpha = (C) + 4(H) + 4(C.H).$$

$$\beta = 2(H) + 2(C.H) - (C.C).$$

$$\gamma = 4(H) + 4(C.H) - (C.C).$$

$$\omega_1 = -(O) + (C.H) - (C.O) - (O.H).$$

$$\omega_2 = 2(H) - (O) + 2(C.H) - (C.O).$$

I have proved ("On the Calculation of Thermochemical Constants," Arnold, 1909) that the following values obtain (under the conditions of Thomsen's thermochemical determinations):— $\alpha = 210.8$ cal., $\beta = 52.5$ cal., $\gamma = 89.0$ cal., $\omega_1 = 29.7$ cal. or 36.4 cal., $\omega_2 = \frac{\alpha}{2} = 105.4$ cal.

Substituting these values we get:—

Molecular heat of combustion of $R-CH_2-CO-R'$ equals—

$$\theta + 2\alpha - 3\beta - \omega_2 = \theta + 421.6 - 157.5 - 105.4 \text{ cal.} = \theta + 158.7 \text{ cal.}$$

Molecular heat of combustion of $R-CH=COH-R'$ equals—

$$\theta + 2\alpha - 2\beta - \gamma - \omega_1 = \theta + 421.6 - 105.0 - 89.0 - 29.7 \text{ (or } 36.4 \text{ cal.} = \theta + 197.9 \text{ cal., or } \theta + 191.2 \text{ cal.}$$

Thus the two formulæ represent different quantities of energy. It follows, therefore, that they cannot represent one and the same chemical individual. To suppose such an oscillation of a hydrogen atom spontaneously to take place is to exempt the phenomenon from the law of the conservation of energy, since every oscillation is accompanied by a change in energy, amounting to at least $(191.2 - 158.7) \text{ cal.} = 32.5 \text{ cal.}$ per grm.-molecule. The difficulty might be evaded by the further assumption that whilst half the hydrogen atoms in a given weight of the body are in the enol phase, the other half are in the keto phase, and that the energy lost by one half is gained by the other, this quantity of energy passing alternatively from one half to the other. But then we run counter to the second law of thermodynamics. I do not make the assumption that a supposition is *ipso facto* worthless if it contradicts one or other of the fundamental laws of thermodynamics, because there is nothing of necessity in either of these laws; they are both empirical, and, so far as the second is concerned, many men of science anticipate, on philosophical grounds, that this law is not of universal application. But inasmuch as Laar's theory of tautomerism does run counter to one or other of these laws, it can hardly be regarded as an explanation of the chemical phenomena in question. It is rather an assertion that such phenomena are beyond explanation in mechanical terms, and belong to a non-mechanical universe. And we are justified in refusing to adopt this view if an alternative theory, equally probable in other respects, and explaining the phenomena thermodynamically, presents itself.

Now, such an alternative does present itself in the now usually accepted theory of dynamic isomerism. According to this theory the two formulæ in each case represent two distinct isomeric bodies, which are assumed to be very easily convertible into one another. In ordinary circumstances a ketone, for example, is a mixture of both keto and enol forms, in equilibrium with one another, the ratio between the weights of the two isomers depending upon the temperature, &c. Any change in the equilibrium, by the removal of one isomer, brings about the conversion of the other isomer into this, until equilibrium is restored. Thus, if a ketone is mixed with a body which reacts with the keto form, as this form is removed by the reaction, so is a proportionate weight of enol converted into keto, the final product being exactly the same as would have been obtained had the body been pure keto. Exactly the reverse process takes place if the added body reacts with the enol form, the final product being the same as would have been obtained had the body been pure enol.

If this theory is true and bodies such as aldehydes and ketones are mixtures of two isomers—the keto and enol forms—then the experimentally determined heat of combustion of such a body should agree with neither that calculated for one form nor that calculated for the other, but should be some quantity greater than one and less than the other. Such, in fact, is what I found in dealing with Thomsen's determinations in my "On the Calculation of Thermochemical Constants." An example will make this quite clear, thus:—

Molecular heat of combustion of acetaldehyde, C_2H_4O :—

Cal.

$$\text{Calc. for } CH_3-CO-H = 2\alpha - \beta - \omega_2 = 263.7$$

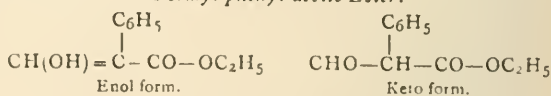
$$\text{Calc. for } CH_2=COH-H = 2\alpha - \gamma - \omega_1 = 286.2 \text{ (at least).}$$

Experimental value (Thomsen) 261.0

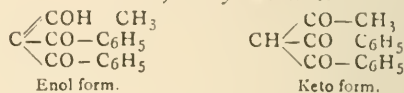
Similar results are obtained in the case of propionaldehyde, iso-butylaldehyde, dimethyl ketone, and methyl propyl ketone, whilst, on the other hand, other carbonyl containing bodies, such as esters, acids, carbonyl sulphide, &c., which do not exhibit either of the phenomena with which I am dealing, give theoretical values in excellent agreement with the experimental.

The theory of dynamic isomerism is not only entirely in agreement with the laws of thermodynamics, but has received important experimental proof in the laboratories of Claisen and Wislicenus, it having been found possible to separate the pure enol and the pure keto modifications in the case of certain bodies, such as formyl-phenyl-acetic ester and dibenzyl-acetyl methane:—

Formyl-phenyl acetic Ester.



Dibenzoyl-acetyl Methane.



The two forms can be readily converted into one another by means of suitable solvents, or simply by heating.* And it is of much importance to note that high temperatures favour the preponderance of the enol form, a fact entirely in agreement with my thermochemical calculations, which show this form to have a higher heat of combustion and therefore to contain more energy than the keto body.

With the substitution of the theory of dynamic isomerism for that of tautomerism (as defined by Laar), a strong support for the mechanical theory of life is knocked away, and arguments of the type quoted from Kekulé lose point. Only apparent and not true spontaneity can be allowed on strictly mechanical principles; life must exhibit no more than this, or be mechanically inexplicable.

I have said that the fundamental laws of thermodynamics are mainly empirical, and that their contravention is therefore within the realm of the possible, if not of the probable. I was, in the foregoing discussion of the phenomena of "double constitution" (if I may so use the term), loth to allow such contravention in the case of phenomena so obviously chemical in nature, and because of the existence of an alternative theory, preferable on experimental grounds, not necessitating this contravention. In the case of life, however, the usually made assumption that the laws of thermodynamics must hold seems to me a little overbold.

There are no laws of nature for which universality can be claimed—laws of nature are not, as some suppose, principles inherent in things—but useful rules invented by man. When a new phenomenon is discovered, or an old one is investigated for the first time, it is wise, of course, to try and use rules which have been found efficient in other cases. But when such rules work badly it is foolish to insist on their employment. Even laws which we are apt to think are axiomatic sometimes break down. Thus we say that the whole is greater than any of its parts; which is indeed true of most wholes with which we have to deal. But mathematicians recognise that the law no longer holds in the region of infinity. The law is not, as we are apt to think, axiomatic or inherent in thought itself; but it is a rule forced on the mind through its experience of the finite. The two infinite series—

$$\begin{array}{l} 1, 2, 3, 4, 5, 6, \&c. \dots \\ 2, 4, 6, 8, 10, 12, \&c. \dots \end{array}$$

obviously contain the same number of terms, since there

* An excellent account of the whole subject from the purely chemical standpoint will be found in Prof. Lachman's "The Spirit of Organic Chemistry," 1904; Chap. IV., to which I gladly acknowledge my indebtedness.

is a one-to-one correspondence between them, each term of the latter being twice that of the former. Yet it is equally as obvious that the second series is part of the first and contains half its number of terms. This is no mere mathematical quibble, but a demonstration that the laws of finite quantity do not apply to infinitude. The law that the whole is greater than its part is not universally valid; but it does serve to distinguish the realm of the finite from the realm of the infinite.

Now, may it not be possible that the fundamental laws of thermodynamics are not universally valid; but serve to distinguish the world of mechanism from the world of life? No adequate experiments, so far as I know, have ever been carried out to prove that the law of the conservation of energy holds for living organisms. We know, of course, that food in some shape or form (*i.e.*, potential chemical energy) is needed by every living organism in order to maintain its activity. But it seems a far cry from this qualitative fact to the quantitative assumption that the amount of energy given out is exactly equivalent to that taken in. Indeed, as concerns man, at least, it is a fact that the largest eaters are very frequently not the most active people; though, of course, when one is dealing with phenomena so complicated many hypotheses to account for them are likely.

Even so astute a thinker as Sir Oliver Lodge (see, for instance, his "Man and the Universe") assumes that the law of the conservation of energy holds for life, and he defines life—that which endows living matter with its characteristic properties—not as a form of energy, but as a director of energy. I admit that this hypothesis has had and still possesses much attraction for me. But I do not know whether even it can be squared with the laws of thermodynamics. How is such directivity effected? Even the pulling of a trigger of a pistol, to use Sir Oliver Lodge's own illustration, requires the expenditure of some energy, however small, and if our souls can pull the triggers of our brains the balance of our energy accounts, if I may so put it, will not work out to zero, as demanded by the law of conservation.

Mr. Hereward Carrington, in a work entitled "Vitality, Fastening, and Nutrition," entirely rejects the orthodox opinion. He places nervous energy in a category by itself as what may perhaps be labelled "psychic energy," which is unobtainable from and inconvertible into ordinary energy. This we receive, according to him, during sleep, and in no way from food. Such a view seems, perhaps, fantastic at first sight; but, really, when we are dealing with phenomena so little understood as those of life, it is well not to dogmatise. Any assumption is as valid as any other, provided it works as well. And, as a matter of fact, this assumption does not necessarily subvert the law of conservation. The independent existence of psychic energy, related to ordinary energy, say, as $\sqrt{-1}$ is to 1,* does not interfere with the law of the conservation of the latter, and may be assumed to follow a law of conservation (or perhaps a law of growth) itself.

So far as the second law of thermodynamics is concerned, however, there is evidence for regarding the phenomena of life, or at least of conscious life, as constituting a universe wherein this law does not obtain. Maxwell's "sorting demon" is, of course, a practical impossibility, but it is a theoretical possibility. And the theoretical possibility that intelligence may contravene this law is destructive of its theoretical universality. So far as practical possibilities are concerned one may venture perhaps to suggest that there is a sense in which the law of evolution is contrary to the law of the increase of entropy (*i.e.*, the second law of thermodynamics) and follows a law of increase of potential, where that means increase in the possibilities of work and utility.

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* With regard to this symbolism, the reader may be referred to my "A Mathematical Theory of Spirit" (Rider, 1912), and a letter contributed by myself to the *Occult Review* for May, 1914 (vol. xix., p. 230) on "The Nature of the Will."

THE DETERMINATION OF NITRIC NITROGEN IN SOILS.*

By E. R. ALLEN.

(Concluded from p. 269).

2. *The Valmari-Devarda Method* of reducing in the presence of MgO was first studied. The nitric nitrogen was introduced as $N/28 HNO_3$ into Kjeldahl flasks, diluted to 300 cc., and 1 gm. MgO and 3 mgrms. alloy added. The flask was then connected with the regular Kjeldahl distilling rack and distillation carried on for thirty minutes, rinsing out the condenser with steam at the end of this period, as has been recommended by Benedict (Note 6). The results, given in Table II., show that the method gives promising results with 5 mgrms. nitric nitrogen, but fails in the presence of 25 mgrms. Since Valmari obtained satisfactory results for 17.5 mgrms. of nitric nitrogen it was surprising that our results were low for 25 mgrms. It at once occurred to us that the alkalinity of the magnesia itself is not sufficient for rapid reduction of this amount of nitric nitrogen and expulsion of the ammonia, but that the increased alkalinity resulting from the reduction of the alkali nitrate used by Valmari might be sufficient to produce quantitative results. In obtaining the data in Table II. the nitric acid added was converted into magnesium nitrate, which on reduction gave rise to insoluble magnesium hydroxide, thus not increasing the alkalinity. The importance of this point was shown in the following experiment, in which the 12.5 cc. $N/7$ nitric acid added were just neutralised with $N/10$ alkali, the magnesium oxide and alloy then added, and the reduction and distillation carried out as before. In five determinations, 25.09, 24.81, 25.05, 24.91, and 24.80 (average 24.93) mgrms. nitrogen were recovered.

TABLE II.—Reduction and Distillation of Nitric Nitrogen in Presence of Magnesium Oxide.

5 mgrms. Nitrogen taken.			25 Mgrms. Nitrogen taken.		
No.	Mgrms. N found.	Ph ₂ NH reaction.	No.	Mgrms. N found.	Ph ₂ NH reaction.
1...	4.956	Faint	1...	23.21	Faint.
2...	4.962	"	2...	23.58	"
3...	5.091	"	3...	23.75	"
4...	4.990	"	4...	22.85	"
5...	5.013	"	5...	23.94	"
Average 5.002			Average 23.46		

These results show that while the alkalinity produced by MgO alone is not sufficient to effect quantitative reduction and distillation of a 25-mgrms. portion of nitric nitrogen in a thirty-minute period, the alkalinity produced as a result of the reduction of an alkali nitrate added to that produced by MgO is sufficient to effect the reduction in this time. In all subsequent operations the standard nitric acid added was neutralised with standard alkali, regardless of whether the reducing solution was made alkaline with MgO or NaOH.

The behaviour of the method in the presence of organic matter was next studied. 300 cc. of the soil extract high in organic matter were measured into Kjeldahl flasks, then 10 cc. of a previously analysed potassium nitrate solution (3.96 mgrms. nitric nitrogen) and 5 cc. of an analysed ammonium sulphate solution (4.98 mgrms. ammonia nitrogen) were added. 1 gm. of magnesium oxide was added, the ammonia distilled off (thirty minutes), and flask and contents cooled; the water distilled off was replaced with ammonia-free water; 3 grms. Devarda's alloy were added and the reduction and distillation proceeded with. The analyses gave 5.05 and 5.16 mgrms. ammonium nitrogen and 0.32 and 0.36 mgrm. nitric nitrogen. After reduction the solutions gave intense diphenylamine

* From the *Journal of Industrial and Engineering Chemistry*, vii., No. 6.

reactions. The very low results for nitric nitrogen confirm Valmari's statement that the method fails in the presence of large amounts of organic matter. Clarification of the extracts with lime and other precipitants, the addition of electrolytes, increasing the amount of magnesia, all effected some improvement, but did not bring the method up to where it could be recommended as a quantitative procedure. An additional difficulty with the magnesia method is the fact that in the presence of organic matter the foaming was very bad and could not be avoided by the addition of such substances as paraffin or crude oil.

The other procedure of the Valmari-Devarda method—*i.e.*, reduction in approximately N/10 NaOH—was next tested in pure solutions and in the presence of organic matter. 2 cc. of our Kjeldahl alkali (50 per cent) added to 300 cc. of water produced an alkalinity slightly above 0.1 normal (10 cc. of this neutralized 11.92 cc. of N/10 H_2SO_4). The procedure was the same as used before except that on account of foaming, even in pure solutions, distillation could be carried on less rapidly, and forty-five minutes were required to distil over 100–125 cc. The solutions, high in organic matter, were boiled for thirty minutes after the addition of the alkali and standard nitric acid in order to expel ammonia. Since there is always danger of some of the fine alkaline spray, produced by the rapid evolution of hydrogen, being carried over, the contents of the receivers were re-distilled over magnesium oxide. In order to show the magnitude of the error so introduced the results of both distillations are reported. 25 mgrms. of nitric nitrogen were added in all cases as N/28 HNO_3 .

TABLE III.—Reduction of 25 Mgrms. Nitric Nitrogen in approximately N/10 Sodium Hydroxide.

No.	First dist.	Second dist.	PH ₂ NH reaction.
<i>In Pure Solution, Mgrms. N found—</i>			
1... ..	24.99	24.73	Faint
2... ..	25.02	24.90	"
3... ..	25.12	25.01	"
4... ..	25.07	24.77	"
5... ..	25.22	24.91	"
Average ..	25.08	24.87	
<i>With High Organic Matter, Mgrms. N found—</i>			
6... ..	24.98	25.06	None
7... ..	24.91	24.90	"
8... ..	24.39	24.73	"
9... ..	24.45	24.49	"
10... ..	24.65	24.63	"
Average ..	24.68	24.76	

Reduction is evidently more complete in the presence of organic matter. The tendency of the results to be lower under these conditions is no doubt due to the slight reducing action of the organic matter during the preliminary distillation period. That there is less alkali carried over in Nos. 6–10 than in 1–5 is to be attributed to the fact that on account of foaming the solutions containing organic matter were distilled more slowly.

The magnesia method of Valmari appears to be reliable if organic matter is absent. The fact, however, that the alkalinity of the magnesia itself is not sufficient to effect complete reduction would suggest that, although very rapid and convenient, the method had best not be indorsed too strongly as yet. It is unreliable in the presence of any considerable amount of organic matter. The Valmari-Devarda method, reducing in approximately N/10 alkali, appears to be the more reliable procedure, and is evidently applicable in the presence of organic matter.

3. *Mitscherlich-Devarda Method.*—The procedure proposed by Mitscherlich and Herz for the reduction of nitric nitrogen differs from the original Devarda method in that

a different distillation apparatus is used. It differs from Valmari's method in this particular, and also in the fact that strongly alkaline solutions are used for reduction and distillation. It is shown later that for reduction a dilute alkaline solution is preferable to the concentrated one used by Mitscherlich, although Mitscherlich has shown beyond a doubt that his method gives reliable results. Furthermore, as mentioned above, reduction in a strongly alkaline solution renders the separation of the nitric and organic nitrogen almost impossible.

Of the procedures tested, then, reduction with Devarda's alloy in dilute sodium hydroxide solution is to be preferred.

Factors Affecting Reduction.—The factors studied were:—1, Concentration of alkali; 2, Amount of alloy; 3, Time. Since MgO solutions are too weak to effect quantitative reduction in the presence of organic matter and solutions N/10 in NaOH are sufficiently strong, and since it is advantageous to keep the concentration of the alkali to a minimum, determinations were made in solutions high in organic matter which had been made approximately N/20 in NaOH. The conditions were otherwise the same as in the set of determinations reported above, in which N/10 NaOH in presence of high organic matter was studied. Only 6.78 and 11.03 mgrms. of nitrogen were recovered from the 25 mgrms. nitric nitrogen added, and the solutions after reduction gave intense reactions for nitrites with Griess' reagent. Hence N/20 NaOH is not sufficiently strong to effect a rapid and complete reduction, while according to Table III. N/10 is sufficiently concentrated. The concentrations between N/10 and N/20 were not studied.

The directions in the literature vary somewhat in regard to the amount of alloy required. Sutton ("Volumetric Analysis," 1910, 10th ed., 285) states that five times the weight of the nitrate should be used. Valmari uses 1 to 2 grms., while Mitscherlich and Herz obtained with 2 grms. the nitrogen equivalent of 23.48 cc. N/50 acid as against a true value of 24.40, while their results quoted above were obtained by the application of 3 grms.; *i.e.*, the amount of alloy which Valmari recommends Mitscherlich and Herz found insufficient. In order to obtain more information on this point the experiments as shown in Table IV. were carried out. The reduction of 25 mgrms. nitric nitrogen was performed in the regular manner in 300 cc. portions of pure solutions.

Nos. 22, 23, and 34 are the values obtained after redistillation over MgO, while the other data were obtained from a single distillation.

The results in Table IV. show that the recommendation to use an amount of alloy equal to five times the weight of nitrate is unsound. The concentration of the alkali is apparently of more importance than the amount of nitrate. The data also clear up the contradictions in the recommendations of Mitscherlich and Herz as compared with those of Valmari. 2 grms. of alloy are insufficient in strong alkali, while this amount is sufficient in MgO solutions, and 1 grm. is sufficient in N/10 solutions. The superiority of N/10 NaOH solutions over more concentrated ones in the matter of the alloy used is apparently due to the fact that in the former case practically all the hydrogen is evolved at 100°, while in the latter case much of it is evolved at lower temperatures. The fact that MgO solutions, in which practically all the hydrogen is evolved at 100°, require more alloy than solutions N/10 in NaOH is perhaps due to the fact that in these extremely weak alkaline solutions more hydrogen is evolved from the larger surface of the larger amount of alloy. At any rate, in view of the data on N/10 NaOH and on strongly alkaline solutions, the former solutions were heated during the reduction as strongly as foaming would permit.

The time required for quantitative reduction of 25 mgrms. of nitric nitrogen was next determined. The 300 cc. of solution contained in a Kjeldahl flask was heated to boiling in minimum time, which in each case was eight minutes. The boiling was continued for the

lengths of time indicated below, the seething solution quickly filtered with suction, and the filtrate tested with diphenylamine:—

	I.	II.	III.	IV.
Minutes boiled ..	0	2.5	5.0	10.0
Ph ₂ NH reaction ..	Strong	Strong	Faint	Faint

The data show that reduction had proceeded sufficiently at the end of five minutes. Optimum conditions for quantitative reduction are, therefore, N 10 NaOH and 1 gm. of alloy, the time required for the expulsion of the ammonia being ample to allow quantitative reduction.

TABLE IV.—Amount of Alloy Required to Reduce 25 Mgrms. Nitric Nitrogen in Presence of Different Amounts of Alkali.

No.	Grms. alloy.	Mgrms. N found.	PH ₂ NH reac.
<i>MgO—</i>			
1.	0.50	a 21.54	Strong
		b 18.07	"
2.	0.75	a 24.91	"
		b 23.38	"
		c 23.42	"
		d 24.56	"
3.	1.00	a 22.42	"
		b 23.45	"
		c 23.52	"
		d 24.91	"
4.	2.00	a 25.00	Faint
		b 25.00	"
		c 25.15	"
		d 25.15	"
<i>N/10 Alkali—</i>			
21.		a 19.03	Strong
		b 22.34	"
22.		a 24.84	Faint
		b 24.62	Strong
		c 25.05	Faint
		d 24.27	Strong
23.		a 24.78	Faint
		b 25.01	None
		c 24.78	Faint
		d 24.81	None
<i>Strong Alkali (a) —</i>			
31.		—	
32.		a 16.48	Strong
		b 15.94	"
33.		a 21.35	"
		b 22.02	"
34.		a 24.39	Faint
		b 24.94	"

(a) 25 cc. of 50 per cent NaOH in 300 cc. Mitscherlich and Herz used 50 cc. of concentrated alkali per 200 cc.

Choice of Distillation Apparatus.—The almost endless number of devices that have been proposed for the distillation and quantitative determination of ammonia may be divided into two general classes. In the first of these the condenser, usually block tin, is cooled with water, and in the second the water cooling is dispensed with, and the ammonia is transferred and absorbed by passing the steam directly into the standard acid of the receiver. Those of the first type are preferable for the carrying out of routine determinations in large numbers where a convenient amount of nitrogen may be taken for analysis, while those of the second type are better suited for refined procedures on small amounts of nitrogen. Obviously, then, a device of the second class is to be preferred for use in determinations of nitric nitrogen in soils in which the amounts of nitrogen dealt with are very limited indeed, and in which every possibility of refinement must be taken advantage of. The most desirable apparatus of this second class is evidently that of Mitscherlich (*Landw. Fahr.*, 1909, xxxviii., 280). The Pannertz (*Treadwell-Hall*, "Analytical Chemistry," 1913, ii., 3d ed., 454) modification of the

original Devarda, and that more recently devised by W. S. Allen (original communication Eighth International Congress Applied Chemistry, New York, 1912, i., 19), are both inferior to Mitscherlich's apparatus, because (1) the scrubbing of the vapours is less complete, and (2) the solubility of the alkali contained in the glass distillation tubes vitiates titrations with N/50 solutions. We therefore adopted for subsequent work the apparatus shown in Fig. 1 (Note 7), which is essentially that of Mitscherlich, and which constitutes Mitscherlich's modification of the original Devarda method.

A few slight modifications have been made in the apparatus. The Hegerschoff distillation bulb used by Mitscherlich is replaced by the Hopkins tube, B; the 250 cc. Kjeldahl scrubbing flask is replaced by the 200 cc. round-bottomed ring-necked Jena flask, D; and the delivery ends of the distillation tubes (C and E) are provided with slight bulb-like enlargements perforated with 1 mm. holes. This last improvement not only insures better scrubbing in flask D and better absorption in flask F, but by producing more even ebullition reduces the danger of spattering. Flask F is a 300-cc. seasoned Jena Erlenmeyer. Mitscherlich and Herz call special attention to the necessity of the distillation tube (E) being made of quartz. Trials with such substances as Jena glass, borate silica Jena glass, and porcelain failed to give satisfactory results. Only when quartz was used were the probable error of distillation and titration kept sufficiently low. Since Mitscherlich and Herz report 366 determinations (*Landw. Fahr.*, 1909, xxxviii., 302) conducted to ascertain the suitability of substances other than quartz, and failed to get a satisfactorily low probable error of the blank distillation with any other material, we accepted their conclusions on this point without further experimentation (Note 8).

Approximately 40 cc. of water are placed in flask D together with a pinch of magnesium oxide and one of magnesium sulphate. The former facilitates the expulsion of ammonia, although Mitscherlich and Herz found it unnecessary (*Landw. Fahr.*, 1909, xxxviii., 306), while when magnesium sulphate is present and spray containing sodium hydroxide is carried over from flask A to D the hydroxyl ions are at once precipitated as magnesium hydroxide, and the probability of alkali being carried into flask F is reduced.

The time required to completely reduce the nitric nitrogen and drive it quantitatively into flask F was determined on 25-mgrm. portions of nitric nitrogen, which were reduced with 1 gm. alloy in N/10 NaOH. The reduction and distillation were carried on for varying periods. The distillation was controlled so as to avoid any danger from loss due to spattering from flask I. Extraneous heat was not applied to flask D.

	I.	II.	III.	IV.
Minutes reduction and distillation	20	30	40	40
Mgrms. nitrogen recovered	24.38	24.74	25.05	25.05

The above data show incomplete recovery in a 20 min. period, doubtful in 30 min., while satisfactory results are obtained in 40 minutes' reduction and distillation. A period of 40 minutes was, therefore, adopted for all subsequent work.

Blank reductions and distillations, using N-free reagents, showed very small amounts of acid neutralised. In ten runs the average was equal to 0.09 cc. of N/50 H₂SO₄, with maximum and minimum values of 0.18 and 0.01 cc. respectively. This shows that no appreciable amount of spray is carried over nor alkali dissolved out of the glass parts of the apparatus.

Probable Error of the Method.—No description or development of a method is complete without some consideration of the accuracy attainable with it, which property of a method is best expressed as its probable error calculated by the method of least squares. The choice of a method for a particular line of investigations is made

somewhat at random unless there is some knowledge at hand relative to the accuracy attainable with the different methods applicable. We have, therefore, devoted some attention to the matter of probable errors, and although our values are calculated from only ten determinations, they serve to show the order of magnitude of the error of the results yielded by the method.

The probable error of the complete method was determined in pure solutions on 5 mgrm. and 25 mgrm. portions of nitric nitrogen, using N/10 alkali in the reducing solution, 1 grm. alloy, and distilling for 40 minutes in the Mitscherlich apparatus.

TABLE V.—Probable Error of Nitric Nitrogen Determination.

No.	cc. N/50 H ₂ SO ₄	Mgrms. nitrogen.	cc. N/10 H ₂ SO ₄	Mgrms. nitrogen.
1.	17.76	4.976	17.80	24.94
2.	17.76	4.976	17.79	24.92
3.	17.76	4.976	17.83	24.98
4.	17.67	4.951	17.81	24.95
5.	17.83	4.996	17.73	24.84
6.	17.73	4.968	17.79	24.92
7.	17.77	4.979	17.78	24.91
8.	17.70	4.960	17.81	24.95
9.	17.70	4.960	17.76	24.88
10.	17.67	4.951	17.82	24.97
Average	17.735	4.969	17.79	24.93
Theoretical value..		5.000		25.00
Probable error ..		±0.009		±0.028
Deviation from theoretical value		-0.031		-0.07

These probable errors are certainly to be regarded as quite small. That obtained with N/50 solutions is of practically the same magnitude as that reported by Mitscherlich and Herz, who used N/50 solutions altogether. Since the reduction is effected in weakly alkaline solutions and will proceed quantitatively in the presence of high organic matter, the method is to be regarded as having attained the aim of this work, and it is believed can later be perfected to a point where it will meet the requirements of a physiological study of nitrification.

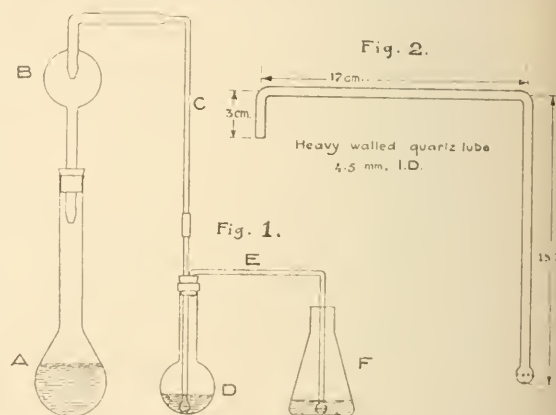
Discussion.

General Considerations.—A few additional points deserve attention in regard to the above results. Apparently too much has been claimed for the aluminium reduction method. Aside from the objection to it that it involves transfer of alkaline solutions containing ammonia, it is certainly more sensitive to some forms of organic matter than is the reduction with Devarda's in solutions N/10 or stronger in NaOH. Reduction in solutions made alkaline with MgO has much to commend it, since the error due to carrying over of spray is avoided, in pure solutions at least; it is very rapid, since the amount of hydrogen evolved is too small to produce foaming, and therefore the reduction and distillation may be performed in 30 minutes. A very large amount of effort was spent in this work in an attempt to obtain a reliable and accurate method by the reduction in the presence of MgO and distillation with an ordinary Kjeldahl rack, a method which would be extremely simple and rapid. The quest was finally abandoned, however, partly because the reduction in presence of MgO is of doubtful value and partly because the Kjeldahl rack itself is less suited for refined work than the apparatus proposed by Mitscherlich and Herz. Of course the MgO reduction might be employed in ordinary soil extracts and the N/10 solutions in those high in organic matter, as originally recommended by Valmar, yet the fact that solutions N/20 in NaOH are unreliable for the reduction in the presence of high organic matter indicates that a very low amount of organic matter would prevent quantitative reduction of nitric nitrogen in MgO solutions which are less than N/1000, and justifies in our

judgment the rejection of this procedure for the determination of nitric nitrogen in soil extracts, where varying and uncertain amounts of organic matter are always present.

Solutions approximately N/10 in NaOH are apparently the lowest alkalinity that can be safely used in reductions with Devarda's alloy in soil extracts. It is superior to reduction in the more concentrated solutions not only in the points mentioned above but because there is less danger of the flask contents boiling over as a result of violent action, and such devices as a water bath (used by W. S. Allen, *loc. cit.*) under the generating flasks may be dispensed with. Using N/10 solutions for reduction and the Mitscherlich apparatus, extremely accurate results are obtained quite easily.

Procedure Recommended.—The procedure finally recommended for the determination of nitric nitrogen in soil extracts, which is to be designated as the Valmar-Mitscherlich-Devarda method, and which is regarded as the most reliable that has yet appeared, in that it combines the strong and eliminates the weak features of each, is as follows:—40 cc. of water, a small pinch of magnesia and one of magnesium sulphate are added to flask D of the Mitscherlich apparatus (Fig. 1); 25 cc. of



standard acid and 60 cc. of neutral redistilled water are placed in flask F; 250 or 300 cc. of aqueous soil extract are placed in a 500 cc. Kjeldahl flask, 2 cc. of 50 per cent sodium hydroxide added, the mouth of the flask closed with a small funnel to prevent spattering, and the contents of the flask boiled for 30 minutes. The water which has boiled off is replaced, and after cooling 1 grm. of Devarda's alloy (60 mesh) and a small piece of paraffin are added, and the flask connected with the apparatus; reduction and distillation are carried on for 40 minutes. The receiver contents are then cooled, four drops of 0.02 per cent solution of methyl-red added, the excess acid is nearly neutralised, the liquid boiled to expel CO₂, cooled to 10–15°, and the titration completed.

Summary.

I. A reduction method is considered to be preferable for the determination of nitro nitrogen in soil extracts. Of such procedures only the modified Devarda and aluminium reduction methods gave promise of meeting our requirements.

II. Reduction with Devarda's alloy in MgO solutions and the aluminium reduction method did not give reliable results in the presence of high organic matter.

III. Reduction with Devarda's alloy in strongly alkaline solutions renders separation of the organic and nitric forms of nitrogen almost impossible, requires a larger amount of alloy than does reduction in solutions N/10 in NaOH, and the reaction is so violent that care must be continually exercised to prevent a loss of the determination.

IV. Reduction with Devarda's alloy in solutions N/10 in NaOH gave reliable results in the presence of high organic matter. It requires a small amount of alloy, the reaction proceeds quietly, and the action of such dilute alkaline solutions on organic matter is very slight. Reduction in solutions N/20 in NaOH is unreliable in the presence of high organic matter.

V. The Mitscherlich apparatus is superior to the other distillation devices for the manipulation of the Devarda method.

VI. The method proposed, which combines the desirable features of the Valmari Devarda and of the Mitscherlich-Devarda procedures, and which is to be designated as the Valmari-Mitscherlich-Devarda method, is the most accurate and reliable that has yet appeared for the determination of nitric nitrogen in soil extracts.

Notes.

1. It should be stated, however, that Mitscherlich and Herz were not concerned with the separation of organic and nitric nitrogen, but only in the question of complete reduction, so that their method for total nitrogen would certainly include all nitric nitrogen.

2. Rupp and Loose. *Ber. d. Chem. Ges.*, 1908, xli., 3905; see also Treadwell-Hall, "Analytical Chemistry," 1913, ii., 3rd ed., 543.

3. All burettes used in this work were made according to the specifications of the U.S. Bureau of Standards, but did not bear the control stamp. Calibration curves by means of a 2-cc. Ostwald pipette showed, however, that the limits of error did not exceed the tolerances permitted by the Bureau of Standards Circular ix., 1913, 16.

4. The term "neutral water" as used in this paper refers to water neutral to the indicator used, i.e., to methyl red. Strictly neutral water (i.e., in which $(H^+) = 10^{-7}$, would of course be alkaline to methyl red.

5. The directions given in Treadwell-Hall (1913, ii., 3rd ed., 543) are to dissolve 0.02 gm. of free acid in 100 cc. of hot water. This recommendation is certainly incorrect, as the above amount of free acid will not dissolve in 100 cc. of water. The free acid is almost insoluble in water, its saturated solution at the ordinary temperature being only about N/100,000, while its alkali salts are very soluble (Tizard, *loc. cit.*, 2485).

6. *Journ. Am. Chem. Soc.*, 1900, xxii., 259. This procedure was used in all distillations reported in this paper, which were performed with the regular Kjeldahl distilling apparatus.

7. All distillations up to this point had been carried out with the ordinary Kjeldahl distilling rack.

8. The tubes which we used were obtained from Hanovia Chemical Co., Newark, N.J., and were made according to specifications shown in Fig. 2, at a cost of 7 dols. 80 cents each. Thin-walled tubes can be purchased at a much lower cost, but because of their fragility are not to be recommended.

Industries of the Empire Fair.—The preliminary prospectus of this Fair, to be held in March, 1917, has just been issued. The Fair, which it is hoped will be of the same benefit to British merchants and manufacturers as the Leipzig Fair to German trade, is not a private enterprise, but is controlled by the principal Trade Associations, and practically every British industry is to be represented. The building will be more than three times the size of any other exhibition building in London, and will be situated at Willesden Green. All the goods exhibited and sold will be of British manufacture, and the sections and sub-sections include Drugs and Chemicals, China and Glass, Grocery, Agricultural and Horticultural Goods, Leather Goods, Stationery, Drapery, and many other classes. Applications for space may be made to Mr. W. Glass, Lincoln House, High Holborn, W.C., from whom further information may also be obtained.

THE SEPARATION OF POTASSIUM AND SODIUM BY THE USE OF ANILINE PERCHLORATE, AND THE SUBSEQUENT ESTIMATION OF THE SODIUM.

By D. U. HILL.

THE chief purpose of the experiments to be described was to determine the availability, as a method for estimating sodium quantitatively, of the precipitation of sodium chloride from solution in alcohol by means of gaseous hydrogen chloride, after the removal of potassium as perchlorate. Kreider and Breckenridge (*Am. Journ. Sci.*, 1896, [4], ii., 263) have determined the delicacy of the qualitative test for sodium made in this way, and have found that "even in 40 cc. 0.0002 gm. of sodium oxide can be seen distinctly; from which fact," they conclude, "it is evident that this method can be applied to the quantitative determination of sodium."

The possibility of substituting aniline perchlorate for perchloric acid as precipitant of the potassium has also been tested in the present investigation. Aniline perchlorate forms crystals of definite composition, without water of crystallisation, so that the amount to be used can be readily determined by weighing. A greater advantage which it was thought the use of the aniline salt would have over the acid, viz., that it could be more easily prepared, proved to be illusory. Aniline expels the ammonia from ammonium perchlorate when the two substances are boiled together, but the reaction is slow, and during the boiling the aniline develops a dark colour. No convenient way of getting rid of this colour could be found. Other methods for preparing aniline perchlorate, starting with the ammonium salt, suggest themselves, as, for instance, the conversion of ammonium perchlorate into barium perchlorate by boiling with barium hydroxide, and then into aniline perchlorate by dissolving in dilute alcohol, adding aniline, precipitating the barium as chloride by hydrochloric gas and ether, and evaporating off the excess of hydrochloric acid; or by mixing exactly equivalent amounts of barium perchlorate and aniline sulphate (Spallino, *Ann. Chim. Applicata*, i., 435; *Chem. Abs.*, 1914, viii., 2701). But all of these methods are more laborious than the preparation of perchloric acid by Willard's method (*Journ. Am. Chem. Soc.*, 1912, xxxiv., 1480), i.e., the oxidation of ammonium perchlorate to perchloric acid by dilute aqua regia. Indeed, the easiest way to prepare the aniline perchlorate is to make the acid first by this very simple method, and then to add aniline to a water solution of the acid until some of the oil remains after shaking, and boil vigorously to expel the excess aniline with the steam before it has time to darken. Colourless crystals are obtained in this way.

Experiments were made first to determine the completeness of the precipitation of sodium chloride from 97 per cent alcohol by gaseous hydrogen chloride. The method was as follows:—0.1000 gm. of purified sodium chloride was dissolved in 1.5 cc. of water, 48.5 cc. of absolute alcohol was added (this amount of 97 per cent alcohol will not hold much more than 0.05 gm. of sodium chloride in solution) and gaseous hydrogen chloride (conveniently evolved by the action of concentrated sulphuric acid upon massive ammonium chloride in a Kipp generator) was passed into the cooled solution through an inverted funnel. When the solution appeared to be saturated with the gas, the precipitate was collected on asbestos in a perforated crucible, dried at about 110°, and weighed. Table I. shows the results of these experiments.

TABLE I.

	NaCl taken.	NaCl found.	Error on NaCl.	Error on Na ₂ O.
	Gm.	Gm.	Gm.	Gm.
1.	0.1000	0.0994	-0.0006	-0.0003
2.	0.1000	0.0989	-0.0011	-0.0006
3.	0.1000	0.0994	-0.0006	-0.0003
4.	0.1000	0.0992	-0.0008	-0.0004

A series of experiments was then made in which both potassium and sodium were estimated. Equal amounts of recrystallised potassium chloride and sodium chloride were weighed out, and dissolved in 1.5 cc. of water. The amounts used are shown in Table II. An excess of aniline perchlorate (about 0.5 grm.) dissolved in 48.5 cc. of absolute alcohol was then added, and the precipitate of potassium perchlorate was filtered off on a perforated crucible with the aid of suction, and washed with about 20 cc. of 97 per cent alcohol. The precipitate was dried at 110° and weighed. The filtrate was saturated with hydrogen chloride from the Kipp generator as in the previous experiments, the precipitate of sodium chloride collected on a perforated crucible, washed with a saturated solution of hydrogen chloride in 97 per cent alcohol, dried, and weighed. The results of this series of experiments are shown in Table II.

TABLE II.

	KCl taken. Grm.	KClO ₄ found. Grm.	Error on K ₂ O. Grm.	NaCl taken. Grm.	NaCl found. Grm.	Error on Na ₂ O. Grm.
1.	0.0500	0.0932	+0.0001	0.0500	0.0496	-0.0002
2.	0.0400	0.0729	-0.0005	0.0400	0.0392	-0.0004
3.	0.0400	0.0727	-0.0006	0.0400	0.0393	-0.0004
4.	0.0400	0.0728	-0.0006	0.0400	0.0394	-0.0003
5.	0.0300	0.0558	—	0.0300	0.0293	-0.0004
6.	0.0300	0.0556	-0.0001	0.0300	0.0295	-0.0003
7.	0.0300	0.0543	-0.0005	0.0300	0.0295	-0.0003
8.	0.0300	0.0540	-0.0006	0.0300	0.0296	-0.0002

The errors on potassium are greater than those obtained by Kreider (*Am. Journ. Sci.*, 1895, [3], xlix., 443), who took pains to convert the potassium chloride completely into perchlorate by evaporating it twice with perchloric acid to a syrup-like consistency, and in washing used 97 per cent alcohol containing perchloric acid, finishing with a very little pure alcohol. In the case of sodium the experimental results indicate the presence of a small constant negative error due apparently to some solubility of sodium chloride in the saturated solution of hydrogen chloride in alcohol, as well as to losses in manipulation. Unfortunately, the error per cent cannot be lessened by working with larger amounts of the salts on account of the limited solubility of the chlorides in alcohol.

During the past two years the methods described above for precipitating potassium by aniline perchlorate, and then sodium chloride by hydrochloric acid gas, have been successfully used as a means of detecting the presence of these elements by the class in qualitative analysis in the Kent Chemical Laboratory of Yale University. In order to lessen the amount of gaseous hydrogen chloride used, the sodium, after the removal of the potassium, is precipitated by means of sulphuric acid instead of hydrogen chloride where possible. A few drops of a dilute solution of sulphuric acid in alcohol will generally precipitate even very small amounts of sodium as sodium sulphate, but if too much acid is added the acid sulphate is formed and dissolved in the alcohol. Hence, if no precipitate is obtained with sulphuric acid, gaseous hydrogen chloride is passed into the solution to saturation, precipitating the sodium as chloride practically completely.—*American Journal of Science*, xl., p. 75.

Faraday Society.—On Wednesday, December 8, the Faraday Society will hold a General Discussion on "The Corrosion of Metals Ferrous and Non-ferrous" at the Institution of Electrical Engineers, Victoria Embankment, W.C. The President, Sir Robert Hadfield, F.R.S., will take the Chair at 8 p.m. The Discussion will be preceded by the reading of Papers by Mr. Leslie Aitchison, Dr. C. H. Desch, Dr. J. Newton Friend, Mr. W. E. Gibbs, Mr. Bertram Lambert, Mr. Arnold Philip, and Mr. S. Whyte, after which the subject will be open to general discussion. The members of the Iron and Steel Institute and the Institute of Metals have been invited to attend the meeting. Others desirous of attending can obtain tickets on application to the Secretary of the Faraday Society, 82, Victoria Street, S.W.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 18, 1915.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"Theory of the Capillary Tube." By Lord RAYLEIGH, O.M., F.R.S.

In a recent paper Richards and Coombs comment on deficiencies in the mathematical treatment of the capillary tube, some of which it is here attempted to remedy. In the best experimental arrangement a wide and a narrow tube are connected below, and the difference between the levels of the lower parts of the two menisci is measured. In the interpretation of the results for deducing the surface-tension of the liquid, two problems arise: (i.) how to allow for the weight of the meniscus in the narrow tube, and (ii.) to find what diameter is necessary for the wide tube in order that the elevation due to curvature of the liquid surface may be neglected.

The first problem was considered by Poisson, but his results in the only really important case, viz., when the liquid wets the walls of the tube, have been disputed. Poisson's formula is here confirmed and extended. If r denotes the radius of the tube, h the measured height of the meniscus above the truly plane level, T the surface-tension, g gravity, and ρ the density of the fluid,—

$$\frac{2T}{g \cdot \rho \cdot r} = h + \frac{r}{3} - 0.1288 \frac{r^2}{h} + 0.1312 \frac{r^3}{h^2},$$

an approximation which should suffice for experimental purposes. It may be remarked that the first two terms on the right correspond to the assumption of a spherical surface, which is legitimate when r is small enough.

A completely adequate solution of the second problem is more difficult. But it is easy to show theoretically that such diameters as are sometimes used for the wide tube (2.5 cm. or 3.0 cm.) are quite insufficient, at any rate in the case of water, a conclusion reached also by Richards and Coombs in direct experiment. It appears further that the widest tube used by these observers (3.8 cm.) would be insufficient to take advantage of the actually achieved delicacy of reading. An approximate calculation of the diameter necessary for this purpose gives 4.7 cm.

"Effect of the Form of the Transverse Section on the Resistance to the Motion of an Elongated Body Parallel to its Length through a Fluid whose Viscosity is not Negligible." By Prof. C. H. LEES, D.Sc., F.R.S.

When a very elongated body moves parallel to its length through a fluid, the resistance due to the viscosity of the fluid varies considerably with the form as well as with the magnitude of the cross-section of the body. Values of the total resistance and of the resistance per unit area of contact with the fluid are given in the following cases:—

(A) Fluid moving through pipes: (1) A pipe of circular section with a concentric core; (2) a pipe of elliptic section.

(B) Long bodies moving through fluids: (1) Body of elliptic section with circular and straight-line sections as limiting cases; (2) body of rectangular section with square and straight-line sections as special cases; (3) body of straight-line section with a projecting keel whose length is along the direction of motion.

In all cases, so long as the fluid is in stream-line motion, the law of resistance can be expressed in a simple form, and it is desirable that measurements of the resistance when the motion is turbulent should be made in order to determine the extent to which these laws may be utilised in practical engineering.

"Method of Estimating Distances at Sea in Fog or Thick Weather." By Prof. J. JOLY, Sc.D., F.R.S.

The method proposed is based upon the different velocities of disturbances in differing media. If aerial and submarine signals are simultaneously emitted at a lighthouse station or lightship the lag of the aerial compared with the submarine sound is about 4.3 seconds to the nautical mile. An approaching ship picking up the signals and measuring the lag to an error even of one second becomes aware of her distance to less than one-quarter of a mile. Similarly wireless signals and submarine signals, or wireless and aerial signals, may be used.

If the faster-moving signals be sent out in groups, the individual signals being spaced to regular intervals—say of one second—and the slower-moving signal be always emitted simultaneously with the first signal of a group, the navigator has only to count the faster signals till the slower signal reaches him in order to estimate his distance from the signal station. In this case the signals themselves tell him his distance, and no actual time measurements are required on board ship.

It is shown that this system enables the mariner to determine his position completely under all circumstances which may arise.

"Method of Avoiding Collision at Sea." By Prof. J. JOLY, Sc.D., F.R.S.

This paper deals with an extension of the method described in the preceding paper for estimating distance at sea to the problem of avoiding collision in fog.

It is shown that if vessels possess the means of emitting a loud and crisp sound signal which can be sent out simultaneously with a wireless or a submarine signal, the determination of distance rendered possible thereby, along with wireless information as to course and speed, will enable the navigator on each ship to determine with certainty (1) whether there is risk of collision or whether there is no risk, and (2) the point upon his own course and the moment at which collision is threatened.

The solution of the problem is based upon the fact that at each instant the rate of mutual approach is the maximum if the ships are advancing so as to collide. A simple geometrical construction, which by its character is unlikely to involve error, enables the mariner to solve the problem immediately the signals are received.

"Flow of Electricity through Dielectrics." By S. W. RICHARDSON.

"On the Kinetic Theory of Gaseous Viscosity and Thermal Conduction, and the Law of Distribution of Molecular Velocities in the Disturbed State." By S. CHAPMAN.

The first object of the paper is to determine the velocity-distribution function $f(u, v, w)$ in a gas in which there are small variations of temperature and velocity from point to point. Both simple and mixed gases are considered; the mixtures are supposed uniform, the study of diffusing mixtures being deferred to a later paper. The molecules are subject only to the restriction of spherical symmetry.

It is assumed that there is a possible solution of the form—

$$f(u, v, w) = \left(\frac{h m}{\pi}\right)^{3/2} e^{-hm \sum u^2} \{1 + F(u, v, w)\}$$

where $F(u, v, w)$ is expansible as a power series in u, v, w (the components of molecular velocity after the mass motion has been subtracted), and a complete formal solution for F is obtained in the paper. Two sequences of functions of u, v, w are chosen whose equations of transfer afford two infinite sets of linear equations connecting the two sets of coefficients in F relating to velocity and temperature respectively. Each coefficient appears as the quotient of two infinite determinants.

In a former paper on viscosity (μ) and thermal conductivity (Δ) an approximate form of F was used; the resulting errors are here examined, and correction factors to my previous formulæ are deduced, expressed as the ratio of a symmetrical infinite determinant to its principal

minor. For the most important molecular models these converge rapidly. My former values of μ and Δ need multiplication by 1.016 and 1.025 for rigid elastic spherical molecules, and the corrections are still smaller for molecules which are n -th power centres of force or attracting spheres. For these three types the factor K in the well-known formula $\Delta = K\mu C_v$ lies between 2.50 and 2.54.

The new formulæ of this paper show very satisfactory agreement with experiment, in particular when the molecular diameters deduced from μ are compared with those obtained from the b of Van der Waal's equation.

PHYSICAL SOCIETY.

Ordinary Meeting, November 12, 1915.

Dr. A. RUSSELL, M.A., Vice-President, in the Chair.

A PAPER on "*The Effect of Electric Oscillations on the Magnetic Properties of Iron, investigated by the Campograph*," by Prof. J. A. FLEMING, M.A., D.Sc., F.R.S., and P. R. COURSEY, B.Sc., was read by the former.

At a meeting of the Society in March, 1915, Dr. J. A. Fleming exhibited an instrument which he called a campograph, for photographing and delineating physical curves. Since then the optical arrangements have been greatly improved, and the point of light travelling over the photographic plate is now extremely small and sharp. With this improved campograph the authors have investigated the effect of electric oscillations on the hysteresis and permeability of iron. The general results are as follows:—

1. When an iron wire is taken slowly through a magnetic cycle and a superposed high-frequency magnetising force is also applied, then, if the maximum value of the slowly periodic longitudinal magnetic force does not exceed a certain value, the effect of the oscillations is to increase the area of the hysteresis loop and to increase the magnetisation at the ends of the cycle.

2. If the slowly periodic force has a large maximum value, then the hysteresis loop is diminished in area, but the maximum magnetisation remains unaltered.

3. The increase in area of the hysteresis loop is generally less for high frequency than for low frequency oscillations, because in the latter case the oscillatory flux penetrates further into the iron wire.

4. If oscillatory currents are passed along the iron wire whilst at the same time the iron is taken slowly through a longitudinal magnetic cycle with continuous current, then when the oscillatory current has a small R.M.S. value the effects are generally similar to those produced by longitudinal oscillatory magnetic forces. If the oscillatory current is relatively large, then their effect is to reduce the hysteresis and magnetisation at the ends of the cycle. This last action is due to the circular magnetisation produced by the longitudinal current, which grips the magnetic molecules of the iron and prevents their longitudinal colineation and reduces also the hysteresis.

The same effect is seen when a longitudinal continuous current is passed along an iron wire.

5. The effect of superimposing on a steady feeble longitudinal magnetic force an alternating magnetic force either by undamped or damped oscillations is greatly to increase the permeability at the ends of the cycle, provided the oscillatory force does not exceed a certain value. Beyond that a diminution sets in.

Photographs of the various effects were shown.

DISCUSSION.

Prof. HOWE thought the paper was a valuable addition to the knowledge of the effects of oscillatory fields on the magnetisation of iron.

Mr. D. OWEN thought the rapidity with which investigations could be made with the instrument was very helpful. One would expect that the effect of a strong

current passed along an iron wire which was magnetised longitudinally would be to remove the longitudinal magnetisation completely. This, however, was not the case. In some experiments he had once performed on the effect of currents along the wire superposed on a longitudinally magnetising force it appeared to be immaterial whether the currents were alternating or direct.

Lieut.-Col. SQUIER admired the instrument. The results would, he thought, repay careful study.

Dr. C. CHREE was reminded by many of the results described of the combined effects of mechanical stresses and magnetic forces. Mechanical oscillations produce many similar effects, and he thought it possible that some of the observed phenomena were due to such mechanical oscillations being set up by the alternating magnetic forces.

Dr. S. W. J. SMITH also thought that the results were mainly due to mechanical oscillations set up by the varying fields. Considerable work has been done on the subject. He quoted several observers who had described very similar phenomena produced by mechanical treatment, and indicated how oscillation of the molecular magnets gave rise to several of the effects.

Prof. FLEMING, replying for the authors, said that it had only been possible to give a very rapid sketch of the phenomena. Many observers had worked on the subject, and he did not think any of the results described in the paper were antagonistic to those already accepted. The principal point of the present paper was, however, to indicate the rapidity and ease with which such experiments could be made by means of the campograph.

Demonstrations of (1) A Hydraulic Analogy of a Wheatstone Bridge; (2) A Lecture Table Method of obtaining Recalescence Curves; (3) The Leeds and Northrup Recorder, were given by Mr. R. S. WHIPPLE.

A Hydraulic Analogy of a Wheatstone Bridge.—The analogy of the flow of water along pipes is frequently used when teaching Ohm's law, but the author does not know of a published description of a simple model. In the model shown glass and indiarubber tubing, with some glass taps, are all that is required. The solution used is water coloured with ink, and this is allowed to flow slowly through the bridge-circuit.

The galvanometer or detector is simply a large air bubble in a horizontal glass tube placed across the bridge arms. A tap is placed in the tube for adjusting the size of the bubble. When the capillary resistance of the tubing on each side of the bridge is equal the bubble stands stationary in the centre of the tube. As soon as the balance of the bridge is disturbed by either partially closing a tap or by introducing another length of tubing by the opening of a tap, the want of balance is shown immediately by the movement of the air-bubbles. Balance is restored by introducing or diminishing the resistance in the opposite arm of the bridge.

Recalescence Experiment.—In his Rede Lecture, Sir J. A. Ewing showed the point of recalescence in a steel wire through which an electric current was passing by the variations in its length, which took place when the critical points occurred.

In his experiment a wire of about two metres in length supported a weight, the vertical movement of which actuated a pointer over a dial. As the wire was heated by the current it lengthened, causing the pointer to fall. At the change point when the temperature fell momentarily the pointer rose, owing to the contraction of the wire, falling immediately afterwards as the wire lengthened with the continual heating. The reverse phenomena occurred when the wire was allowed to cool. The only novelty in the experiment shown was in the addition of a camel-hair brush attached to the pointer at the suggestion of Mr. W. H. Aphorpe. The brush is filled with ink and allowed to write upon a drum. The movements of the extremity of the wire are then drawn upon the drum and the point of recalescence shown.

Leeds and Northrup Curve Drawing Recorder.—The Leeds and Northrup recorder is in its main principles not dissimilar to the Callendar instrument, but is modified in many important details. In the Leeds and Northrup recorder the relay is entirely mechanical. The coil is provided with a short boom at right angles to the face of the coil, which hangs untouched in the zero position. When the coil is deflected, owing to a want of balance in the bridge, the boom is gripped mechanically by a lever in the position in which it is resting. As a result of this grip a simple mechanism is brought into action, which moves a slider over a bridge wire, and thus increases or diminishes a resistance in the bridge circuit. Two of the gripping levers are provided, so that the boom is gripped either by the right or left hand one depending on the side to which the coil is deflected.

The details of the mechanism were illustrated by a series of lantern slides.

BRITISH ASSOCIATION OF TRADE AND TECHNICAL JOURNALS.

A BUSINESS Luncheon of the British Association of Trade and Technical Journals was held on Friday, November 19, at the Trocadero Restaurant, when there was a large attendance of members. Mr. S. Charles Phillips, Chairman of the Association, presided. The Right Hon. Sir Albert Spicer, Bart., M.P., who was announced to deliver an address on "Some Industries Stimulated by the War; Their Present and Future Development," sat on his right, and the Hon. Sir George Perley, K.C.M.G., on his left.

In the course of his interesting address, Sir ALBERT SPICER said: The special industries about which I want to say something this afternoon are those which were represented at the recent British Industries Fair at the Agricultural Hall in May. They include toys and games, the glass trade, fancy goods, cutlery, silver and electros, clocks, jewellery, paper, stationery and printing. They are all industries which met with severe competition from Germany and Austria. For the time being that competition has ceased, and there is an opportunity for this country to begin anew. The British Industries Fair was a new departure, and one on which the Board of Trade are to be congratulated. They were not great primary industries, but rather secondary industries. The Exhibition was a great success. I took a great deal of trouble to find out the price of a good many things as compared with the price at which they had been sold before the war. The question which was occurring to one was what can be done to retain the hold we are getting on these industries now after the war; we may take it that, at any rate for some time to come, Germany and Austria will not have a look in, but at the same time we must reflect that when the war is over these two countries will again become keen competitors, and perhaps stronger competitors in the neutral markets of the world; and in all our plans to retain these industries we must bear that fact in mind and must not increase the price so as to be shut out from these neutral markets.

Now the war has come, and all these industries have a new start. In considering what can be done to retain and increase them, we must look at the question from two sides. First of all there is what the Government can do. As to that I am precluded from saying anything because I am a member of a Sub-Committee of an Advisory Committee on Commercial Intelligence to the Board of Trade. We have taken a good deal of evidence, but we have not yet considered our report. But there is a good deal we can look at from the point of view of the manufacturers and traders. I do not think that in the past we have done all that we might have done. I do not think our principals have been so well educated for their work as those of many of the German firms. (Hear, hear.) We must produce better educated men in our trades and industries. At one

time we were ahead of the other nations of the world in our commerce, and we allowed ourselves to be spoiled by that real success. The first thing I would suggest with regard to the future is that we should make all our organisations much more complete, so that we can help each other in matters that are really of common interest to us all, without interfering with the individual firms or the competition that must exist between different firms. I believe that there are a great many matters that we can consult together about, and that we can strengthen one another. I have been surprised as I have heard some of the evidence submitted to us how at a given moment if the various firms in the same business had united for some new departure which individually they were not strong enough to bring about, a most successful achievement might have been accomplished. Then I think in matters of research and experiment, we have at the present time our modern universities, and a committee has been set up now for the first time, the chairman of which is Sir William McCormick, under the Board of Education, who want to receive information from manufacturers as to how the Government may be of use to them.

One of the difficult questions we have to combat is that of getting skilled labour. The days of apprenticeship are over, and we shall have to do something to try and meet the deficiency. We have throughout the country a great many technical institutes, and we must look to these to help. Arrangements must be made by which the education shall be given in working hours, because the training done outside ordinary hours, when naturally young men and women are tired with their day's work, is not so profitable. (Hear, hear.) Then we must get more help with regard to railway rates and shipping freights. I do not think that as a whole we get fair play in these matters. (Hear, hear.) Possibly we are to blame, because we have not worked together sufficiently. Had we co-operated more, we might have made it more worth while of the railway companies to give us lower rates.

As I said, I cannot touch at present on what the Government may do in the future, but there is one thing I should like to say—I give it as my personal opinion—that after the war it ought to be decided that no article required by the Government for the conduct of war should be imported from a foreign country. It is a source of weakness—and has been a source of weakness during the war—that we have had to depend on other countries, and whether it can be done by protecting trade, or by Government making the goods themselves, something should be done. In these few observations I have endeavoured to place before you a few common lines in which I think we can help to retain some of those industries which are extremely busy now, but as regards which we shall have to meet great competition afterwards. In bringing these points before their readers the trade and technical papers can render valuable help, and have a great part to play. (Applause.)

SIR GEORGE PERLEY said: I was very pleased to come here to-day on the invitation of your Chairman, for various reasons. In the first place my trade happens to be one that his paper is interested in. I am in Canada what you call a timber merchant—a manufacturer of timber and lumber. I have followed that occupation through my whole life, and to-day, of course, we have naturally gone over to the side of paper-making. I was rather diffident as to coming here when I knew I was to speak before the editors, managers, and owners of so many journals. Even a man like myself, who has been in public life many years, has to take off his hat to newspapers. This Association has a great power for good; there is no question about that. Business journals everywhere take a great part in the development of trade, and have proved their usefulness not only in the British Isles but in every part of the world; and I know that at this particular juncture you are helping all you can. As to a Commercial Ministry for this country, I would not like to make any remarks—it is outside my jurisdiction. I do not know whether the

details of our Department in Canada would be suitable here, but I know that we have at the head of our Department one of our best men, Sir George Foster. In connection with it there are many things beside the cultivation and encouragement of trade in itself. I know something about it because I carried out the duties for some months during the absence of Sir George Foster. For instance, I remember, during that winter passing an Act through Parliament dealing with the hall-marking of silver—a very technical subject which I found very great difficulty in understanding myself. Then we have to do with the grain standards—a thing we are very jealous about, because the standards of our wheat are well known throughout the world. We have a Grain Board which takes charge of that subject under the Department of Trade and Commerce, and in the year that I had the privilege of carrying on that Department we started several Government elevators in the North-West in order to relieve the congestion and enable the farmers to market their produce in that way if they thought fit. Then the Department has to do with subsidies to steamships. We have lately started a new line from Canada to the West Indies, which is closer to Canada than to this country, with the idea of encouraging trade. I am happy to say that the results so far have been satisfactory.

I have the honour of representing Canada in London at the moment. I am a member of the Canadian Cabinet. I am not High Commissioner, but am carrying on the duties as a member of the Cabinet, and have been here eighteen months. Happening to be here when the war broke out, I have stayed here to do what I can in the interests of Canada and the Empire, particularly in matters relating to the great war. (Applause.) In common with the other Dominions Canada is endeavouring to do her share—(hear, hear)—and we can claim that as far as men and money are concerned we have done very well. (Hear, hear.) It is our intention to continue to do so. (Applause.) It is our war. We are part of the British Empire. In fact, the words "British Empire" perhaps carry to us even greater significance than to those who live in these islands. We are very proud of the Anglo-Saxon heritage of liberty and democratic institutions, and shall always be ready to fight to maintain them. We are hoping that this dreadful war is going to bring the different parts of the Empire closer together. (Hear, hear.) It is making us know each other better, and will help to consolidate the Empire. We believe we shall find in the Anglo-Saxon race enough ability to find a solution under which every part of the Empire shall have something to say in matters of common interest, such as peace and war and our foreign relations. (Hear, hear.) That is an ambition we very properly hold, and I believe this war will help us to realise it. This will also bring us closer together in our business relations, and I believe there is no body of men more able to help in this than those I see around me. I appeal to you to do all you can in that direction. A great deal of the business which has hitherto been done by the enemy nations must fall into other hands. In these islands you will no doubt get a large part of it, and what you cannot do yourselves I ask you to pass on to the overseas dominions in preference to any neutral country. (Applause.) Let us keep all the trade we can within the Empire, and in that way we shall get the benefit at both ends. Canada is becoming a great manufacturing country, not only producing an immense quantity of wheat, but also of raw material, while at the same time developing our manufactures, and we think it would be to the benefit of you as well as ourselves that you should utilise as much as possible. I ask your help in that direction. Trade and technical journals can do a lot for us, and you need not fear but that we on our side will do all the business we can with the Mother Country. I wish you all every success. (Applause.)

MR. PERCIVAL MARSHALL, in proposing a vote of thanks to Sir Albert Spicer, said: The two admirable addresses to which they had listened had shown that the industries

of Great Britain had opportunities of winning through if they were backed by energy, resource, and courage. That was the message which they as the business Press of the country had to pass on to their readers. It might seem to some of their guests that the gathering was a small one, but it was a larger one than it seemed to the eye, because at least sixty business papers were represented there; and if they took the average circulation as 3,000 copies, it would be seen that the two gentlemen had been addressing an audience of 300,000 business men. They were a young association, but were doing a great work. They had achieved at least one great piece of work, and had two others in hand. They played a great part in getting the injustice of the proposed postal changes removed; they were moving in the matter of a proposed Ministry of Commerce and had presented a petition to the Prime Minister. They had under consideration the regularising of the relations between trade journals and advertising agents. They felt very hopeful that some good and tangible results would follow from their efforts.

The resolution having been carried with much enthusiasm, the CHAIRMAN pointed out that Mr. Marshall underestimated the number of journals represented, he putting the figure at 100, with an audience of nearer 1,000,000.

NOTICES OF BOOKS.

Chlorine and Chlorine Products. By GEOFFREY MARTIN, Ph.D., D.Sc., F.C.S. London: Crosby Lockwood and Son. 1915.

THIS book contains concise accounts of the preparation and purification of chlorine and chlorine products, bromine, iodine, and hydrofluoric acid. The Weldon and Deacon processes of preparing chlorine are discussed first, but it is pointed out that in the United States and Germany electrolytic processes are rapidly superseding them, and to these special attention is given, emphasis being laid upon the serious aspect of British manufacturers' neglect of these important methods. A chapter is devoted to the preparation of liquid chlorine, the use of which for the dissemination of poisonous gas has been adopted by the Germans in war, and the manufacture of chlorates, bleaching powder, and hypochlorites is discussed. The theory of electrolytic bleaching is explained, and some apparatus which has been successfully used for producing electrolytic bleaching liquids is described. A short account is given of modern oxidising agents—peroxides and persalts is given in a final chapter by G. W. Clough, B.Sc.

The Coals of South Wales, with Special Reference to the Origin and Distribution of Anthracite. By AUBREY STRAHAN, M.A., Sc.D., LL.D., F.R.S., and W. POLLARD, M.A., D.Sc., F.I.C. Assisted by E. G. RADDLEY. Second Edition. Printed for His Majesty's Stationery Office by Jas. Truscott and Son, Ltd., Cannon Street, E.C. 1915.

THIS monograph gives the results of an investigation into the characters of the coals of South Wales, which was carried out during the period 1901–1914. The results of a very large number of analyses are given, together with some account of the analytical methods employed. The special object of the investigation was the study of the origin and distribution of anthracite, and the monograph contains to plates showing lines of equal anthracitism in each seam or group of seams. In the second edition many new analyses have been added, and the new data obtained have led to slight alterations in some of the charts, while the general conclusions of the first edition have been confirmed.

CORRESPONDENCE.

COMFORTS FOR THE SICK AND WOUNDED.

To the Editor of the Chemical News.

SIR,—I beg to say that I should be very grateful if you would allow me through your columns to thank all those who have been kind enough to help me by ordering plants from my Wenlock garden. By this means I have been able to realise over £120, which I propose to spend on comforts for sick and wounded. I beg to say I am engaged in collecting sandbags for instructional purposes by the wish of my superior, General Mends. Any sandbags of the right dimensions, as sanctioned by the War Office, in Hessian or black canvas, would be most gratefully received by me at the address below, and I would forward the same, with name and address of the kind donor, to Headquarters at York in due course.—I am, &c.,

CATHERINE MILNES GASKELL.

Thornes House, Wakefield,
November 18, 1915.

CHEMICAL PRODUCTS WANTED.

To the Editor of the Chemical News.

SIR,—We are writing to ask whether you could give us the names of manufacturers of the undermentioned goods, as we have an order to place for same:—Metabisulphite, phosphate of ammonia, tannin of alcohol.—We are, &c.,

THE BUREAU OF AMERICAN MANUFACTURERS
IN EUROPE, Ltd.

25, Cannon Street, London, E.C.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxi. No. 14, October 4, 1915.

Mutual Solubility of Copper and Lead.—B. Bogitch. —When lead is added to copper the product is heterogeneous, and the alloy separates into two layers, one rich in copper and the other in lead. It has been suggested that this separation is merely due to the difference of the densities of the two metals which separate at the moment of solidification, and that in the fused state they would be miscible in all proportions. Other investigators assert that when fused together they form a double layer like water and ether. The author has studied the question experimentally, and finds that the double layer is formed when the percentage of copper lies between 34.5 and 87. The liquid double layer exists only between the temperature of the solidification of the upper layer 940° to 975°, above which there is no difference in the composition of the liquid.

MEETINGS FOR THE WEEK.

MONDAY, 6th.—Royal Society of Arts, 4.30. (Cantor Lecture). "Optical Glass," by W. Rosenhain.

Society of Chemical Industry, 8. "Use of Graphical Methods in the Solution of Problems in Technical Chemistry," by F. G. Donnan. "Transport of Material in the Form of Dust," by T. C. Cloud. "Sampling and Analysis of Beeswax," by M. S. Salamon.

WEDNESDAY, 8th.—Royal Society of Arts, 4.30. "The Art of Finding your Way at Night without a Compass," by Lieut.-Col. W. A. Tilney.

Faraday Society, 8. General Discussion on "The Corrosion of Metals."

THURSDAY, 9th.—Royal Society, 4.30. (The Croonian Lecture). "The Respiratory Process in Muscle, and the Nature of Muscular Motion," by Dr. W. M. Fletcher and Prof. F. G. Hopkins.

"International Atomic Weights, 1916"—In our last issue, p. 270, the figures for Nitron should be 222.4 and for Sodium 23.00.

THE CHEMICAL NEWS.

VOL. CXII., No. 2924.

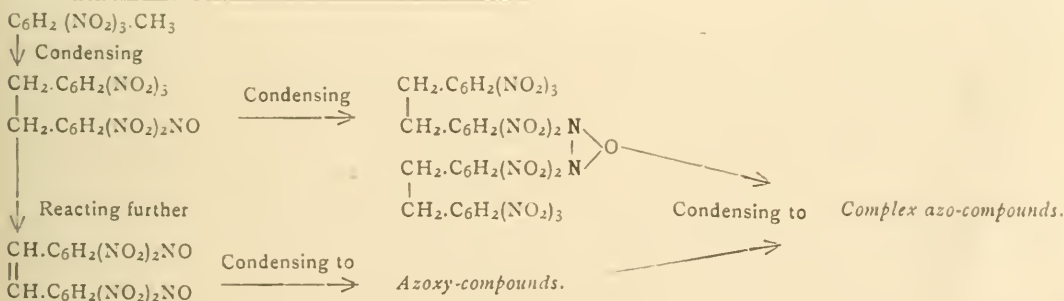
THE ACTION OF ALKALIS ON TRINITROTOLUENE.*

By MAURICE COPISAROW, M.Sc.,
Honorary Research Fellow, Chemical Department, The University,
Manchester.

As there was a tendency at one time among some manufacturers to free the crude trinitrotoluene from acid by means of alkalis, the problem of the action of alkalis on T.N.T. may be of some interest.

The work of Perkin¹, Klinger², Bender and Schultz³, Fischer and Hepp⁴, Lobry de Bruyn and Von Leent⁵, Korczynski⁶, Green⁷, and Hantsch⁸, with their collaborators, Bush and Kogel⁹ and Will¹⁰, on the action of alkalis on trinitrobenzene and *p*-nitrotoluene, with its numerous *o*-substitution products, including trinitrotoluene, has proved the following facts:—

1. The reactive sensitiveness of nitro-groups towards alkalis increases with their accumulation in the molecule.
2. The sensitiveness and number of chemical changes is greatly augmented by the presence of an alkyl-radicle in *p*-position, facilitating probably the formation of nitroic acids.
3. The reactivity of the molecule is very much increased by the introduction of electronegative groups in *o*-position to the alkyl radicle.



The nature of the reaction between alkalis and the nitro-bodies is only partially cleared up so far, but the accumulated data are more than sufficient to prove that the reaction is of a very profound nature.

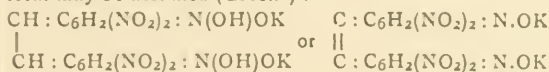
A whole series of reactions pass rapidly one after another, and although some of the intermediate bodies cannot be isolated, still with some care certain of them may be oxidised and in this manner isolated before further condensations have taken place. The reactions result in—

- (a) The formation of addition compounds;
- (b) " " substitution " ;
- (c) " " condensation " .

Trinitrotoluene forms addition-compounds with hydrocarbons, phenols, and amines; it forms salts with potassium cyanide $\text{C}_6\text{H}_2\cdot\text{CH}_3(\text{NO}_2)_2\text{NO}(\text{CN})\text{OK}$ (Hepp¹¹), with caustic potash $\text{C}_6\text{H}_2\cdot\text{CH}_3(\text{NO}_2)_2\text{NO}(\text{OCH}_3)\text{OK} + \text{H}_2\text{O}$, and with ammonia $\text{C}_6\text{H}_2\cdot\text{CH}_3(\text{NO}_2)_2\text{N}(\text{NH}_2)(\text{ONH}_4) : \text{O}$ (Korczynski⁶) (the ammonia and potash were used in a methyl alcoholic solution), which are regarded by Hantsch⁸ as salts of nitroic $-\text{R}\cdot\text{NO}(\text{OH})_2$ and nitroic-

ester $-\text{R}\cdot\text{NO}(\text{OR}')\text{OH}$ acids, formed by the addition of water or alcohols to trinitrotoluene.

But the formation of nitroates constitutes only the first stage of the reaction, as immediately they are formed substitution takes place, dinitrotoluidines being produced from T.N.T. by the action of alcoholic ammonia, and dinitrohydroxybenzoic acids from trinitrobenzoic acids by the action of hot water, the hydroxy-group being replaced by a methoxy, under the influence of methyl-alcoholic potash (Körner and Contardi¹², Giua¹³). In presence of alkalis the substitution products react further, a whole series of condensations taking place, nitronitrosodibenzyls and nitronitrosostilbenes being formed, which in the form of nitroic salts undergo further condensations to azoxy and azo-compounds. In the case of the salts of the dibenzyl and stilbene derivatives the tautomeric quinoid form may be assumed (Green⁷) :—



The general mechanism of the condensations is represented in the accompanying scheme, the compounds being actually present in the form of quinoid salts.

With careful oxidation we may isolate hexanitrodibenzyl and hexanitrostilbene. *a*-Trinitrotoluene reacts easily with sodium carbonate, baryta, and lime-water in the cold (in an alcoholic or acetone solution), giving a deep red coloration. Treating an alcoholic solution of trinitrotoluene with sodium bicarbonate we may observe a change of colours passing from violet through purple to deep red.

Will (*loc. cit.*) found that β - and γ -trinitrotoluene are still more sensitive, reacting with 1 per cent solution of sodium carbonate and lead oxide, forming derivatives of tolyl oxide. Green (*loc. cit.*) studied the relative influence exerted by *o* substituting groups on the reactivity of

p-nitrotoluene by observing the relative temperature at which the colour formation commences under constant conditions of alkalinity and molecular concentration, and obtained the following results:—

Substance.	<i>o</i> -Substitution.	Coloration produced.	Minimum temperature of reaction.
<i>p</i> -Nitrotoluene	H	Crimson	78°
" <i>o</i> -xylene	CH ₃	"	79—80°
" <i>o</i> -tolylmethyl-ester ..	OCH ₃	"	75—77°
" <i>o</i> -toluidine ..	NH ₂	"	81°
" <i>o</i> -toluic acid ..	COOH	"	78—79°
<i>o</i> -Chloro- <i>p</i> -nitrotoluene	Cl	Violet	23—24
Phenyl- <i>p</i> -nitro-toluene- <i>o</i> -sulphonate	SO ₃ C ₆ H ₅	Blue	about -20
<i>p</i> -Nitro- <i>o</i> -cyanotoluene	CN	"	" -20
2:4 dinitrotoluene ..	NO ₂	"	below -20

The writer, to compare the reactivity of 2:4:6 trinitrotoluene, containing two strongly negative groups in *o*-position to the alkyl-radicle, with those quoted by Green, performed the following experiment, using Green's method:—

* See "Trinitrotoluene," CHEMICAL NEWS, cxii., 247.

0.166 grm. of pure 2.4.6 trinitrotoluene were dissolved in 1 cc. of pyridine and 5 cc. of pure methyl alcohol. To the solution, which was kept in solid CO_2 + ether, 5 cc. of a saturated solution of KOH in methyl alcohol (about 33 per cent KOH), cooled in the same manner, were added, the mixture being stirred with a thermometer and the minimum temperature at which coloration appeared noted.

The following result was obtained:—

Substance.	Coloration.	Minimum temperature.
2.4.6 .. T.N.T.	Orange-red changing to deep red ..	below -65

It must be noted that the salts formed by the action of alkalis on trinitrotoluene are highly explosive. Lobry de Bruyn³ found that the potassium salt of trinitrobenzene, $[\text{C}_6\text{H}_3(\text{NO}_2)_3\text{MeOK}]_2 + \text{H}_2\text{O}$, explodes on heating on a platinum foil.

Dupré¹⁴ found that the addition of a little caustic potash caused T.N.T. to explode when heated to 160°C .

References.

1. *Journ. Chem. Soc.*, 1880, xxxvii., 546.
2. *Ber.*, 1883, xvi., 941.
3. *Ber.*, 1886, xix., 3234; 1895, xxviii., 422; 1910, xlii., 3602.
4. *Ber.*, 1893, xxvi., 2231; 1895, xxviii., 2281.
5. *Rec. Trav. Chim.*, 1895, xiv., 89, 95, 150.
6. *Bull. Acad. Sci. Cracow*, 1908, 633.
7. *Ber.*, 1897, xxx., 3097; 1898, xxxi., 345, 1078; *Journ. Chem. Soc.*, 1904, lxxv., 1424, 1432; 1907, xci., 2076; 1908, xciii., 1721.
8. *Ber.*, 1899, xxxii., 628, 1317; 1910, xlii., 2119.
9. *Ber.*, 1911, xlii., 1549.
10. *Ber.*, 1914, xlvii., 704.
11. *Annal.*, 1882, ccxv., 360.
12. *Atti R. Accad. Lincei*, 1914 (v.), xxiii., II., 464.
13. " " " " " 484;
13. " " " " " 484;
13. " " " " " 484;
14. *Annual Reports of H.M. Inspectors for Explosives*, 1903, 26.

THE CONDUCTIVITY AND VISCOSITY OF SOLUTIONS OF ELECTROLYTES IN FORMAMID.*

By P. B. DAVIS, W. S. PUTNAM, and HARRY C. JONES.

THE work of Jones and his collaborators in the field of non-aqueous solvents and in mixtures of these solvents with one another thus far included a comprehensive study of both the conductivity and viscosity of typical salts in methyl and ethyl alcohols, in acetone, and in glycerol, as well as in binary and ternary mixtures of these solvents with one another and with water. A review of all this work is to be found in Publication of the Carnegie Institution of Washington, No. 210, chapter 7.

Because of the somewhat limited solubility of electrolytes in most organic solvents the scope of this work has necessarily been somewhat limited in the case of the pure liquids themselves. This is especially true with acetone and the alcohols. Glycerol, however, notwithstanding its high viscosity, proved to be a remarkably good solvent.

Among the few remaining liquids suitable for such work, the one used in this investigation—formamid—is perhaps the most important.

The fact that it has been studied so little in the past must be attributed to the difficulties encountered in ob-

taining a product pure enough for conductivity purpose and to its relatively high price.

Previous Work in Formamid.

Until quite recently no investigation of the physical chemical properties of this remarkable liquid had been made. A brief sketch of the recent work is given below.

In his preliminary paper on organic solvents Walden mentions the marked similarity of formamid to water as compared with other liquids in its solvent action on inorganic salts, and in later papers he records some of its physical constants in comparison with other amids and with water, viz., the dielectric constant and association factors (*Zeit. Phys. Chem.*, 1906, xlvii., 145, 175), specific conductivity, and molecular conductivity of the normal electrolyte $\text{N}(\text{C}_2\text{H}_5)_4\text{I}$ (*Ibid.*, 1905, liv., 179) and the viscosity (*Ibid.*, 1906, lv., 230). All of these constants were obtained with a product which, as will be shown later, was far from pure, although it may be pointed out that the first two constants are not appreciably affected by small changes in the purity of the solvent.

Turner and Merry (*Journ. Chem. Soc.*, 1910, xcvi., 2076) in their work on the molecular composition of trivalent nitrogen compounds, pointed out that the high association factor of formamid is one of its most striking characteristics, and they observed its similarity to water. They noted also that the association of formamid diminishes more rapidly with rise in temperature than that of water, and suggested that the solvent power for salts was largely due to its high molecular complexity. Somewhat later Walden (*Zeit. Phys. Chem.*, 1910, lxxv., 555), in a study of the temperature coefficient K , for organic liquids in the Ramsay and Shields equation for molecular surface-tension, found that in the case of formamid the value was far below that for non-associated liquids (2.12), having only the value $0.594 - 0.710$, and from these data obtained an association factor in close agreement with that as determined by Turner and Merry (*loc. cit.*).

Dunstan and Kassel (*Zeit. Phys. Chem.*, 1911, lxxvi., 367), while determining the fluidity of various binary mixtures, measured the viscosity of mixtures of formamid and *i*-amyl alcohol at both low and somewhat elevated temperatures, and noted a pronounced minimum in the fluidity curves at about 60 to 70 per cent of formamid at both temperatures, and also a slight maximum at about 10 to 20 per cent formamid for the lower temperature.

Rohrer (*Zeit. Elektrochem.*, 1910, xvi., 420) studied the solvent properties of formamid for organic salts, and also the electrolysis of its solutions. He compared the density with that of water above the freezing-point and found no minimum, as in the case of the latter, but that the solvent expanded linearly with rise in temperature, the variation of the specific volume being represented by $V = 0.8674 \times (1 + 0.000742 t)$.

Rohrer also found that, according to Faraday's law, copper dissolves in formamid at all dilutions, half as univalent and half as bivalent ions at the anode, and obtained a good separation of copper with a weak current, but with a stronger current the metal separated as a dark slime.

Similar results were obtained with lead, zinc, and tin. With all of these metals in air more metal dissolved at the anode than separated at the cathode. The electrolysis of nickel, cobalt, iron, aluminium, and magnesium salts yielded no appreciable amount of metal at the cathode.

Rohrer also noted the formation of metallic formamides, and also of crystalline double compounds, which will be considered in discussing the properties of formamid as compared with those of water.

In a quite recent paper Walden (*Bull. Imp. Acad. Sci.*, St. Petersburg, 1911) gives an account of his cryoscopic work in this solvent. In his preliminary discussion he states as his reason for adopting the freezing point rather than the conductivity method for measuring dissociations that the high specific conductivity of the solvent (as

* This investigation was carried out with the aid of a grant from the Carnegie Institution of Washington to H. C. Jones, and will form a part of its Publication No. 230. From the *Journal of the Franklin Institute*, November, 1915.

	Molecular weight	TABLE I.	
		Water 18.	Formamid 45.
Melting-point		0°	1·5—2·1 (Walden).
Boiling-point 760 mm.		100°	200 212.
Density 0°/4°		0·9999	1·151 (Walden, Davis).
Dielectric constant		81 (Drude) 25 .	84 (Walden).
Association factor 30°		3·81 (Ramsay-Shield).	6·18 (Turner and Merry).
K—surface tension 20—30°			0·65 (Turner and Merry).
Minimum specific conductivity		4 × 10 ⁻⁸	2·8 × 10 ⁻⁶ (Davis and Putnam).
Average specific conductivity working values		1·5 × 10 ⁻⁶	2·7 × 10 ⁻⁵ (Davis and Putnam).
Viscosity 25°		0·00891 (Thorpe and Rodger).	0·0324 (Davis).
Dissociation of N(C ₂ H ₅) ₄ I at V=100		91 per cent .	{ 93 per cent (Walden). 98 per cent (Davis and Putnam).

measured by him) rendered it impossible to obtain accurate data by the latter method. However, as will be pointed out later, by our method of preparation formamid with a specific conductivity comparable with that of water, may be obtained with a loss of material only one-third that experienced by Walden.

Walden determined the freezing-point constant of formamid, and gives the value 35·0 as the mean of six determinations, using urea, acetic ester, diethylsulphite, ethyl acetate, mesityl oxide, and nitraniline respectively as the solute.

He also studied the dissociation of a number of electrolytes, including salts and both strong and weak acids, and pointed out that all binary salts are strongly ionised at relatively high concentrations; the ionisation increasing slowly to the limit $\alpha=100$ as in water, the limit, however, being reached at a smaller dilution in formamid.

The same was found to hold for acids except in the case of those where combination took place between solvent and solute, as in the case of some of the strong acids, the values found being smaller than those for water.

Formamid as a Solvent.

Formamid is a clear, colourless, and somewhat viscous liquid, melting at about 18°, and boiling under atmospheric pressure with partial decomposition at 200 to 212°. It reacts neutral to litmus and is quite hygroscopic, undergoing a slow hydrolysis at ordinary temperature into ammonium formate.

This solvent is the most closely allied to water in its properties of all the organic solvents. The two are miscible in all proportions, neither being soluble to any extent in absolute ether, chloroform, benzol, hexane, &c., nor do they dissolve appreciably the aromatic hydrocarbons, nitrobenzol, fats, oils, &c.

Further similarity may be traced in their solvent action on metallic salts, thus: in the cold, cobalt and nickel salts yield solutions in formamid, similarly coloured with those in water, although in some instances the formamid solutions undergo change in colour on warming, which is probably due to a predominance of the unionised salt, since formamid undergoes a much sharper decrease in association with rise in temperature than water.

As Walden has pointed out, the similarity between water and formamid is still more wide-reaching. Phosphorus and sulphur are practically equally insoluble in both, while iodine gives a brownish yellow solution. Starch is also soluble in formamid with formation in concentrated solution of a jelly, and on addition of formamid solution of iodine the starch solution turns intensely blue. The colour, however, is less permanent than in water, owing to the slow action of the iodine on the solvent. The fluorescent dyes also exhibit like phenomena in formamid and in water, this being particularly marked in the case of cosin.

Bruni and Manuelli (*Zeit. Elektrochem.*, 1905, xi., 554) further show that just as water hydrolyses the salts of weak bases, such as those of bismuth and antimony, forming unstable basic salts, formamid by a process of amidolysis may form basic salts of these same metals, and Rohler (*Ibid.*, 1910, xvi., 418), in extending this work, has

isolated characteristic basic salts of copper, cobalt, nickel, and zinc. He also obtained amidates similar to hydrates, of which $\text{PbCl}_2 \cdot \text{HCONH}_2$ is an example, as well as metal formamidates having the general composition $\text{Me}(\text{HNCOH})_2 \cdot 2\text{HCONH}_2$, where Me may be either copper, nickel, cobalt, or zinc.

In addition to the above, Rohler has noticed the formation of well-defined crystalline compounds of formamid with the halogen acids corresponding to the well-known mono, di, and tri-hydrates.

As is now a well-established fact, the dielectric constant of the solvent is a measure of its own association, and therefore a measure of its dissociation power for electrolytes. Of the common solvents water has the highest dielectric constant, and is the best dissociant. Formamid, however, has a higher dielectric constant than water, as will be shown by referring to the table of physical constants of the two solvents (Table I.), and should therefore be a better dissociant, which will be pointed out in our discussion.

(To be continued).

RADIOMETRIC MEASUREMENTS OF THE IONISATION CONSTANTS OF INDICATORS.*

(SECOND COMMUNICATION).

By M. G. PAULUS, J. F. HUTCHINSON, and HARRY C. JONES.

AN investigation of the ionisation constants of methyl-orange and phenolphthalein has already been published in the *Journal of the American Chemical Society* (1915, xxxvii., 776; see also *CHEMICAL NEWS*, 1915, cxii., 195 *et seq.*) by Shaeffer, Paulus, and Jones. In this paper a new method, based upon the absorption of light by solutions of indicators, was developed for the determination of the constants of indicators. It was shown that this method serves as well for a two-coloured as for a one-coloured indicator. The work recorded herein is to be regarded as a continuation of the original investigation, and the purpose is to test the applicability of the method to the determination of the ionisation constant of rosolic acid. A description of the apparatus used has already been given in detail in the original paper.

Theoretical Discussion.—Considering, first of all, that rosolic acid is monobasic (the behaviour of rosolic acid as a dibasic acid will be discussed later), the ionisation constant K_i is expressed by the simple equilibrium equation—

$$\frac{(\text{H}^+)(\text{In}^-)}{(\text{HIn})} = K_i \quad \dots \quad (1).$$

If, then, the hydrogen ion concentration of the indicator solution is fixed, the ratio $(\text{In}^-)/(\text{HIn})$ at equilibrium can be determined. It has been shown in the original paper (*loc. cit.*) that the percentage transmission of a solution, such

* This investigation has been carried out with the aid of a grant from the Carnegie Institution of Washington to H. C. Jones. From the *Journal of the American Chemical Society*, xxxvii., No. 7.

as that of rosolic acid, containing two absorbing components is given by the equation—

$$\ln(I/I_0) = -Kc - K'c_1 \quad \dots (2),$$

where c and c_1 are the concentrations of the two absorbing components, and K and K' are constants depending upon the nature of the absorbing components and the wave-length of light employed. Applying this equation to rosolic acid, let c represent the concentration of the red

component, or $(\ln)$ in Equation 1, and let c_1 represent the concentration of the yellow component or $(H\ln)$. Equation 2, then, will represent the percentage transmission for some given depth of an incompletely transformed solution of rosolic acid. In a solution containing a large excess of acid, $c=0$, and Equation 2 becomes—

$$\ln(I/I_0)' = -K'c_1 = -K'T \quad \dots (3),$$

If a large excess* of alkali is added to the indicator solution $c_1=0$, and Equation 2, reduces to—

$$\ln(I/I_0)'' = -Kc = -KT \quad \dots (4),$$

where T equals the total concentration of the indicator in solution. If the percentage transmissions are determined for the same depth of solution and for the same wave-length of light, and if the total concentration of the indicator is the same in all solutions, then the values of the constants K and K' given by Equations 3 and 4 can be substituted in Equation 2, whence—

$$T \times \ln(I/I_0) = \ln(I/I_0)' \times c + \ln(I/I_0)'' \times c_1 \quad \dots (5).$$

Since the total concentration of the indicator T is always equal to the sum of the two components, $T=c+c_1$, Equation 5 reduces to—

$$c/c_1 = \frac{\ln(I/I_0) - \ln(I/I_0)''}{\ln(I/I_0) - \ln(I/I_0)'} \quad \dots (6).$$

The ratio $c/c_1 = (\ln)/(H\ln)$ can be determined from Equation 6. (I/I_0) is the percentage transmission for some given depth of the incompletely transformed solution under investigation, for some wave length of light; $(I/I_0)'$ the percentage transmission of the indicator solution completely transformed into the yellow component for the same wave-length, and $(I/I_0)''$ the percentage transmission for the same depth of indicator solution completely transformed into the red component, for the same wave-length of light. The total concentration of the indicator in these three solutions must, of course, be the same, but the total concentration need not be known.

Returning now to Equation 1, the method of obtaining all the data necessary for calculating the ionisation constant is known, except that for determining the concentration of the hydrogen ion. This was fixed by solutions of disodium phosphate containing varying amounts of hydrochloric acid. The addition of hydrochloric acid converts the hydrophosphate ion almost quantitatively into the dihydrophosphate ion. The hydrogen ion concentration is given in such a solution by—

$$H^+ = \frac{1.95 \times 10^{-7} (H_2PO_4)}{(HPO_4)} \quad (a) \quad \dots (7).$$

(a) The value of the constant was taken from the work of Abbott and Bray (*Journ. Am. Chem. Soc.*, 1909, xxxi., 760).

If we represent by a , the concentration of the added hydrochloric acid, and by b , the concentration of the disodium phosphate, then Equation 7 becomes—

$$H^+ = \frac{1.95 \times 10^{-7} \times a a_1}{(b - a) a_2} \quad \dots (8),$$

where a_1 and a_2 represent, respectively, the dissociations of the mono- and disodium phosphates present at equilibrium.

* By "a large excess" is meant sufficient alkali to convert the indicator entirely into its red component.

If the quantity of disodium phosphate in the solutions investigated is always kept the same, the hydrogen ion concentration can be varied simply by the addition of different amounts of hydrochloric acid. In this case, the total salt concentration is constant. This is extremely desirable, as it has been shown by Rosenstein (*Journ. Am. Chem. Soc.*, 1912, xxxiv., 1128; see also *Ibid.*, 1915, xxxvii., 804), that neutral salts have a great effect upon the fraction of the indicator transformed. The value of the ionisation constant in the case of phenolphthalein is doubled by increasing the total salt concentration from 0.03 to 0.40 N.

Preliminary Work on Rosolic Acid.—Three stock solutions were prepared, all solutions being made up at 20° with conductivity water. The stock solution of disodium phosphate was prepared from a pure sample of standard make. Its concentration was 0.1036 gm. molecules per litre, the concentration being determined gravimetrically as magnesium pyrophosphate. The concentration of the stock solution of hydrochloric acid was 0.08085 N. The stock indicator solution was prepared by dissolving about 0.4 gm. of an excellent sample of rosolic acid in 2 litres of conductivity water. The total quantity of the indicator did not dissolve, but as has been previously explained, it is not necessary to know the concentration of the indicator employed.

The incompletely transformed solutions to be tested were prepared from the stock solutions, so that all contained the same amounts of indicator and disodium phosphate, but different amounts of hydrochloric acid. This procedure was followed to keep the total salt concentration the same in all solutions. The volume of each solution was 100 cc. The percentage transmissions (I/I_0) were taken with a 20 mm. depth of each solution, and for the same five wave-lengths of light. As explained in the original article (*loc. cit.*), the percentage transmissions were determined by a differential method, which avoided the necessity of introducing certain correction factors due to the glass ends with which the cells were provided.

A consideration of Equation 6 will show that the method of calculating the ratio of the red to the yellow component of any incompletely transformed indicator solution, not only depends upon the transmission of the solution under investigation, but also upon the transmission of an indicator solution containing a large excess of acid in which the indicator is totally transformed into its yellow constituent, and also upon the transmission of an indicator solution containing a large excess of alkali in which the indicator is totally transformed into its red component. Table I. gives the results of a series of measurements made upon the indicator solution containing an excess of alkali. All solutions contain 50 cc. of the stock solution of rosolic acid, plus the amount of N NaOH indicated in the table, the solutions being in all cases diluted to 100 cc. The percentage transmissions are given for five wave-lengths of light between $\lambda = 0.56 \mu$ and $\lambda = 0.58 \mu$, which is the region of the spectrum employed throughout this investigation. In certain cases the results of duplicate measurements are given, which indicate in a general way the accuracy of the results.

Column 2, Table I., gives the percentage transmissions of an indicator solution containing 0.5 cc. N NaOH, the transmissions being determined within a short time after the solution was prepared. Columns 3 to 7, inclusive, give the percentage transmissions after the same solution had stood for various intervals of time up to fifty-five minutes. Columns 8 and 9 give the percentage transmissions of new indicator solutions containing the same amount of indicator and alkali, after these solutions had stood, respectively, for five to twenty-four hours. It will be observed that the percentage transmissions for any given wave-length of light become constant after the solutions have stood between one and five hours.

The fact that solutions of rosolic acid containing an excess of alkali become less and less transparent to yellow light on standing, clearly indicates that the con-

TABLE I.
(I/I_0)—depth of solution = 20 mm.).

1	2	3	4	5.	6.	7.	8.	9.	10.	
	0.5 cc. N NaOH.									
$\lambda = A.U.$	After 5 mins.	After 10 mins.	After 20 mins.	After 30 mins.	After 55 mins.	After 5 hours.		After 24 hours.		3.0 cc. after 24 hours.
5598	22.6	16.1	12.5	10.7	9.08	7.55	6.25	6.37	6.53	9.16
5648	36.1	30.6	27.4	22.6	20.0	20.0	17.0	16.7	17.6	19.1
5698	52.3	44.8	44.2	38.8	37.9	37.0	34.5	34.5	32.2	35.6
5748	64.8	60.6	58.3	55.6	52.8	51.4	52.4	50.7	49.3	50.7
5798	77.0	73.3	71.1	68.4	64.1	64.8	66.6	66.2	63.5	66.3

centration of the red component (Iu) present is becoming greater and greater with a resulting decrease in the concentration of the yellow component (IHu), since the greater the concentration of the red component the more opaque the solution becomes to yellow light.

According to the most recent views (*Am. Chem. Journ.*, 1908, xxxix., 537, 650, 651) concerning the cause of colour production of indicators of the aurine type, the colour is not due simply to the presence of a quinoid group as such, but to an inter- or intramolecular combination of the metallic phenolate with the quinoid complex. It is very probably true, in the case of rosolic acid, that this combination between the metallic phenolate and the quinoid complex takes place rather slowly, with a corresponding intensification of the red colour.

It will be observed that the transmission values recorded in Column 10, Table I., of an indicator solution containing 3 cc. N NaOH are considerably higher than those recorded in Columns 8 and 9, for a solution containing 0.5 cc. N NaOH. In both cases the solutions have come to equilibrium, since it has been shown that equilibrium is established after the solutions have stood between one and five hours. When very much larger amounts of alkali are added (say, 10 cc.), a very perceptible bleaching takes place. In solutions, then, containing an excess of sodium hydroxide two opposing reactions take place; first, a gradual intensification of the red colour brought about very probably by a time reaction between the metallic phenolate and the quinoid complex, and, second, a bleaching of the red colour which is greater the larger the amount of the alkali added. Since it is necessary to know the true percentage transmission (I/I_0)' of a solution completely transformed into the red component, in order to determine the ratio c/c_1 (see above), it follows that the bleaching must be avoided. This result can be obtained by keeping the concentration of the alkali as small as possible, only adding sufficient to transform completely the indicator. The obvious method was to increase gradually the hydroxyl ion concentration until the solutions were shown to be completely transformed. Table II. gives the results of such a determination. All solutions contain 50 cc. of the stock solution of indicator, plus the amount of disodium phosphate and hydrochloric acid indicated in the table. All solutions were allowed to stand a sufficient length of time for equilibrium to be established.

TABLE II.
(I/I_0)'—depth of solution = 20 mm.

$\lambda = A.U.$	1. 25 cc. Na_2HPO_4 , 1 cc. HCl. After 24 hrs.	2. 25 cc. Na_2HPO_4 , 0.5 cc. HCl. After 48 hrs.	3. 25 cc. Na_2HPO_4 , 0 cc. HCl. After 48 hrs.	4. 25 cc. Na_2HPO_4 , 0 cc. HCl. After 96 hrs.
5598	4.44	4.35	4.68	4.76
5648	13.7	14.0	11.1	11.0
5698	22.8	22.8	19.4	18.8
5748	40.0	40.0	33.3	34.9
5798	51.6	51.0	48.4	49.4

Solution 1, Table II., in which the hydrogen ion concentration is 0.8266×10^{-8} gives higher values for the percentage transmissions than Solutions 2 and 3, in which the hydrogen ion concentrations are, respectively, 0.4157×10^{-8} and 0.043×10^{-8} . This shows that Solu-

tion 1 is not completely transformed, since an increase in the red component and a corresponding decrease in the yellow component make the solution more opaque to yellow light. Solution 2 must, however, be completely transformed, since, when the hydrogen ion concentration is still further increased as is the case in Solution 3, the transmission values remain the same. The values of the percentage transmissions recorded in Columns 2, 3, and 4 are the values to be substituted for (I/I_0)' in Equation 6.

In order to ascertain if this same decrease in the transmissions, corresponding to an increase in the red component, would take place on standing with solutions of indicators which are incompletely transformed, four solutions were prepared containing in 100 cc.:—50 cc. rosolic acid, 25 cc. Na_2HPO_4 and 1 cc., 5 cc., 10 cc., and 15 cc. of HCl respectively.

In Table III. are given the percentage transmissions for a depth equal to 20 mm. of the above series of solutions. The transmissions were determined after the solutions had stood for intervals of five, sixteen, and twenty-four hours. The transmission values recorded in Columns 1 and 3 were determined with the same series of solutions. A new series of solutions were prepared for the sixteen-hour determination, the results of which are recorded in Column 2. Solution 1 was not made up for this determination. Duplicate measurements are given in every case.

TABLE III.
(I/I_0)—depth of solution = 20 mm.

$\lambda = A.U.$	1. After 5 hours.		2. After 16 hours.		3. After 24 hours.	
Solution No. 1.—Containing 1 cc. HCl + 25 cc. Na_2HPO_4 .						
5598	16.7	16.3	—	—	4.44	4.35
5648	32.7	30.2	—	—	13.7	14.0
5698	42.8	43.2	—	—	22.8	22.8
5748	59.1	57.4	—	—	40.0	40.0
5798	69.7	70.3	—	—	51.6	51.6
Solution No. 2.—Containing 5 cc. HCl + 25 cc. Na_2HPO_4 .						
5598	30.8	30.8	25.7	25.0	26.4	26.4
5648	39.3	39.6	35.4	35.9	37.5	35.7
5698	52.6	51.7	48.3	40.0	50.0	49.3
5748	66.1	64.5	60.8	60.7	60.3	59.4
5798	72.7	74.3	71.0	71.0	70.7	70.6
Solution No. 3.—Containing 10 cc. HCl + 25 cc. Na_2HPO_4 .						
5598	49.0	49.0	50.7	50.7	49.0	49.1
5648	57.8	57.8	60.0	59.3	60.0	58.8
5698	66.7	68.3	68.7	68.7	70.6	70.6
5748	73.8	73.4	78.5	77.7	76.2	77.4
5798	83.3	83.6	84.2	84.2	84.4	83.0
Solution No. 4.—Containing 15 cc. HCl + 25 cc. Na_2HPO_4 .						
5598	66.1	67.3	68.0	67.2	67.3	67.8
5648	72.4	74.1	74.9	74.3	76.4	76.4
5698	81.6	80.3	81.3	80.4	81.0	79.5
5748	83.2	83.2	87.2	87.2	85.5	85.5
5798	88.2	89.4	90.2	90.2	87.7	87.8

An examination of the transmission values recorded for Solutions 1 and 2, Table III., show that a decrease in the transmissions of incompletely transformed solutions of

rosolic acid also takes place on standing. Solution 2, in which the hydrogen ion concentration (see *ante*) is 4.484×10^{-4} , has come to equilibrium between five and sixteen hours, as is shown by the fact that the transmission values become constant after sixteen hours. In Solutions 3 and 4, in which the hydrogen ion concentrations are, respectively, 10.53×10^{-4} and 19.52×10^{-4} , equilibrium was established before standing five hours. This points to the conclusion that in the incompletely transformed solutions of the indicator the more alkaline the solution the greater the time before equilibrium is established.

(To be continued).

ELECTRO-PLATING WITH COBALT.

A RIVAL TO NICKEL.

IN pursuance of a systematic effort to develop the industrial use of cobalt, of which Canada possesses rich supplies, the Mines Branch of the Canadian Department of Mines has had elaborate investigations carried out at Queen's University, Kingston, Ontario, with the object of discovering the possibilities of the metal as an electro-plating agent. The work was carried out by Dr. Herbert T. Kalmus, with the assistance of Mr. C. H. Harper and Mr. W. L. Savell, and from a report that has just been issued the results seem very promising.

Some 16 different types of solutions or baths were investigated, and while several were found suitable for commercial use two stood out pre-eminent; one was a solution of 200 grms. of cobalt-ammonium sulphate in a litre of water, equivalent to 1.45 grms. of the anhydrous salt in a litre, while the other consisted of 312 grms. of cobalt sulphate and 19.6 grms. of sodium chloride, with boric acid nearly to saturation, in 1000 cc. of water. Both these solutions, according to the report, are substantially self-sustaining once they are put into operating condition, and the amount of ageing required for this purpose is much less than that for the present commercial nickel baths.

Cobalt plates from these solutions on brass, iron, steel, copper, tin, German silver, lead, and Britannia metal articles, of different shapes and sizes, deposited under conditions identical with those met with in general nickel plating practice, are firm, adherent, hard, and uniform. They can readily be buffed to a satisfactory finished surface, having a beautiful lustre which, although brilliantly white, possesses a slightly bluish cast. Plates on various stock pieces satisfactorily withstood the various bending, hammering, and burnishing tests to which commercial nickel work is ordinarily submitted. These solutions are remarkable for their "throwing" power; that is, they readily deposit the cobalt in the indentations of the work.

Rapidity of Working.

The electrical conductivity of these solutions being considerably higher than that of the standard commercial nickel solutions, they may, other things being equal, be operated at a lower voltage for a given speed of plating. The first can plate on the various sizes and shapes of objects met with in commercial practice at a speed at least four times, and the second at a speed at least 15 times, as great as that of the fastest satisfactory nickel solutions. They work at these high speeds in a perfectly still solution, without agitation of any kind, and are cleaner (that is, free from creeping salts and precipitated matter) than the standard commercial nickel baths. The deposit at these high speeds is much harder than the nickel deposited in any commercial nickel bath, and consequently a smaller weight of cobalt deposit will give the same protective coat as a greater weight of softer nickel. With the second solution, working at 150 amperes per square foot on automobile parts, brass stampings, &c., a sufficient weight of cobalt to stand the usual commercial tests, including buffing and finishing, is deposited in one minute. With

the best nickel baths, one hour, at about 10 amperes per square foot, is required to deposit an equally satisfactory plate. Therefore the actual weight of metal on the cobalt plate must be approximately one-quarter that of the nickel. It follows that if nickel is worth 2s. per lb. in the anode form, cobalt could be worth nearly 8s. per lb. in the same form, to be on the same basis, weight for weight of metal.

Other Advantages.

In addition cobalt has other advantages. A plating-room dealing with the same amount of work would be smaller than with nickel, and with the use of mechanical appliances these rapid solutions would reduce the time required for plating as well as the labour costs, while the cost of supplies and repairs would also be less. The voltage for extremely rapid cobalt plating is greater than is required for most nickel-plating baths, but is not so great but that the machines at present in use may generally be employed. For a given amount of work the power consumption is less than for nickel, the amount of metal deposited being less, while the voltage at which it is deposited is not correspondingly greater.

Ornamental work on brass, copper, tin, or German silver would require only a one-minute deposit and even wares exposed to severe atmospheric influences or friction could be admirably treated with cobalt by means of the second solution in 15 minutes. Thick deposits from these solutions are, the authors of the report say, vastly superior to any they have seen produced from nickel solutions. The tendency to distort thin cathodes is less pronounced, while electrotypes and electro-dies have been given a superior thick deposit in a most satisfactory manner, the lines being hard, sharp, and tough and the surface smooth.—*Times Engineering Supplement*.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Anniversary Meeting, November 30, 1915.

ADDRESS OF THE PRESIDENT, SIR WILLIAM CROOKES, O.M.

SINCE our last Anniversary Meeting the Royal Society has lost many of its Fellows. Too long is the list of those who have passed. If my references to their work is brief you will understand that it is due to the exigencies of time, and not to lack of appreciation. No words of mine are necessary to perpetuate the memories of men whose names will live among those of the great masters of Science.

In April this year one of our oldest Fellows, WILLIAM GRYLLS ADAMS, Emeritus Professor of Natural Philosophy at King's College, London, died after a life of great scientific activity at the age of seventy-nine. He was Professor of Natural Philosophy and Astronomy at King's College, London, from 1865 to 1906, and was elected a Fellow of the Royal Society in 1872. His researches covered a wide field, and he was the author of many memoirs in various branches of physics. In 1875 he delivered the Bakerian Lecture on the forms of equipotential curves and surfaces and lines of flow, and in the same year he published an important paper on the change of resistance produced by magnetisation in iron and steel. He made an exhaustive investigation of the effect of light in reducing the resistance of selenium, and devised a new form of measuring polariscope. In later years he made a special study of terrestrial magnetism, and he also published papers on the Illumination of Lighthouses. He was one of the founders of the Physical Society, and was its President from 1878 to 1880. He was also President in 1884 of the Institution of Electrical Engineers, and his inaugural Address on the growth of electrical science and the testing of dynamo machines and incandescent lamps

was a valuable contribution to our knowledge. He served on the Council of the Royal Society from 1882 to 1884, and again from 1896 to 1898.

Dr. R. ASSHETON, who was one of the most eminent of British zoologists, died on October 24, from heart failure following influenza. Dr. Assheton has been described as the first experimental embryologist in England, and his new and original methods enabled him to correct some of the erroneous views of the older school of embryologists. His premature death, when his intellectual powers were still undiminished, is a heavy blow to science, and it will be felt nowhere more than at Cambridge, where he had recently been appointed lecturer in animal embryology.

The death of HENRY CHARLTON BASTIAN, which occurred on November 17, removes from our midst a physician of eminence who will be remembered as the energetic champion of a theory of the spontaneous origin of life. He was at one time Professor of Pathological Anatomy, and afterwards Professor of the Principles and Practice of Medicine at University College, London, and was also consulting physician to the National Hospital for the Paralysed and Epileptic. He was the author of many articles and monographs on paralysis, aphasia, and speech defects, and diseases of the nervous system.

In Sir ARTHUR HERBERT CHURCH we have lost one whose position in the world of science was unique. He was a man of many and diverse gifts and interests, and was an artist of no mean skill and a recognised authority upon precious stones and porcelain. While Professor of Chemistry at the Royal Agricultural College, Cirencester, he did valuable work in agricultural chemistry—being, for example, the first to describe turacin, an animal pigment containing copper. He was also interested in mineralogy, and was the discoverer of the native cerium phosphate Churchite. In 1879 he was appointed Professor of Chemistry at the Royal Academy of Arts, and he then turned his attention to researches on paints and pigments, publishing a standard work on the subject entitled "The Chemistry of Paints and Painting." He conducted an enquiry into the condition of the Frescoes in the Houses of Parliament and the stonework of Westminster Abbey, in which his artistic and archaeological knowledge was invaluable. Sir Arthur Church, who died on May 31, was elected a Fellow in 1888.

In May the death occurred of MORGAN WILLIAM CROFTON, who, after a brilliant career at Trinity College, Dublin, was for three years Professor of Natural Philosophy at Queen's College, Galway, and afterwards Professor of Mechanics and Mathematics at the Royal Military Academy, Woolwich. On his resignation in 1884, he was appointed to a Fellowship of the Royal University of Ireland. Dr. Crofton, who was elected a Fellow of the Royal Society in 1868, was the author of papers on mechanics and geometry, but is perhaps best known for his work on Probability, upon which subject he contributed an article in the ninth edition of the "Encyclopædia Britannica."

DAVID DOUGLAS CUNNINGHAM, who died in December, 1914, rendered great services to science and to the State by his studies of tropical diseases generally, and of cholera in particular. From 1869 to 1879 he devoted all his energies to the investigation of cholera from a pathological point of view, and in 1879 he was appointed Professor of Physiology at the Medical College at Calcutta, where his gifts and the charm of his manner won him great success as a teacher of Indian students. Besides his work in pathology Cunningham carried out numerous researches in cryptogamic botany, and made exhaustive studies of the diseases of plants and of snake venom, and he also made time to perform the duties of many public offices in India. He was elected a Fellow of the Royal Society in 1899.

The death of JAMES GEIKIE, the younger brother of Sir Archibald Geikie, is a great loss to science and to his many friends. When quite a young man he took an active part in the Geological Survey of Scotland and published

many papers giving the results of his observations. He afterwards went to Gibraltar with Andrew Ramsay, the Director of the English Geological Survey, to prepare a report on its water supply. In 1874 he published the first edition of his famous book "The Great Ice Age." In 1882 he was appointed Murchison Professor of Geology and Dean of the Faculty of Science at Edinburgh, and thenceforward he devoted himself chiefly to teaching and the preparation of the many valuable educational works which bear his name. He was one of the founders of the Royal Scottish Geographical Society and was its President for some time. He was a highly successful and inspiring teacher, and was one of Edinburgh's most distinguished scientific men.

Sir WILLIAM RICHARD GOWERS, who died on May 4, had won an international reputation in medicine. His researches dealt chiefly, but by no means exclusively, with neurology. He studied the diseases of the heart and blood-glandular organs, and was the inventor of an instrument for determining the amount of hæmoglobin in blood. In 1880 he published his work on the "Diagnosis of Diseases of the Spinal Cord," and the following year a book on Epilepsy founded on his observations made at the National Hospital for the Paralysed and Epileptic, where he held the post of physician. His chief work was the admirable and widely used "Manual of Disease of the Nervous System." He was elected a Fellow of the Royal Society in 1887 and knighted in 1897.

Dr. ARTHUR SHERIDAN LEA, who died in March at the age of sixty-one, was one of the founders of the Cambridge Physiology School, his research work dealing chiefly with the chemical changes of food during digestion, and the action of rennet and fibrin ferments. He was a Fellow of Gonville and Caius College, and was appointed University Lecturer in 1884. Unfortunately his active career was prematurely cut short by spinal disease, and his later years had been spent in retirement and rest, although he followed with unabated interest the work of his friends and pupils.

RICHARD LYDEKKER, who was one of the most prolific writers upon zoology and natural history, died in April of this year. His first scientific work was connected with the Geological Survey of India, and he made a very thorough study of the zoology and geology of Kashmir. Afterwards he devoted himself more to palæontology, and between 1885 and 1887 he was engaged on the preparation of a catalogue of fossil mammals in the Department of Geology of the British Museum, while some years later he spent some time making a study of the fossil vertebrates in the La Plata Museum. From 1896 until his death he was occupied with the reorganisation of the Mammalian Exhibition Galleries of the Natural History Museum, in which he achieved conspicuous success. A very rapid worker, he published an enormous number of technical and popular articles, and he also co-operated with Sir William Flower in "An Introduction to the Study of Mammals," and edited the "Royal Natural History."

It was with deep regret that we heard that Professor RAPHAEL MELDOLA died suddenly on November 16th at the age of sixty-six. Prof. Meldola was an eminent authority upon the manufacture of coal-tar colours, having worked for many years in the colour works of Messrs. Brooke, Simpson, and Spiller, where he had made important discoveries of new methods and processes. In 1885 he became Professor of Chemistry at the Finsbury Technical College. He was a member of the recently appointed Advisory Council for the Organisation and Development of Scientific and Industrial Research, and was an ardent advocate of the necessity of fostering pure research in order to arrest the decline of industry in this country. He was the author of valuable text-books upon the Chemistry of Photography and the Chemical Synthesis of Vital Products, and also translated and edited Weismann's "Studies in the Theory of Descent." He was elected President of the Chemical Society from 1905 to 1907, Fellow of the Royal Society in 1886, and Davy Medallist in 1913.

We were much grieved to learn that the renowned zoologist, Professor EDWARD ALFRED MINCHIN, had passed away, and the gap he leaves in the scientific world will long be unfilled. In spite of the handicap of ill-health in his youth Minchin was very successful at Oxford, where he was finally elected Fellow of Merton College. After spending some time in research work at foreign marine zoological stations he returned to Oxford as assistant to Sir Ray Lankester and demonstrator of comparative anatomy, and in 1899 was appointed to the Jodrell professorship of zoology at University College, London. Subsequently, he became the first professor of protozoology at the University of London, and director of protozoology at the Lister Institute of Preventive Medicine at Chelsea. In 1911 he was elected a Fellow of the Royal Society. The value of his research in zoology has been fully recognised both in this country and abroad, and in the branches which he made specially his own he had no rival. The refinement of his methods, his accuracy and attention to detail were inimitable, and he put a high ideal of carefulness and thoroughness before his pupils. He published a valuable text book, "An Introduction to the Study of the Protozoa," which has come to be regarded as the standard work on the subject, and he wrote articles in the scientific journals and the "Encyclopædia Britannica," and was an important contributor to Lankester's "Treatise on Zoology." A man of striking originality and of great gifts, he will be deeply mourned by his many friends.

Dr. HUGO MÜLLER, whose death occurred on May 23, was elected a Fellow in 1866. He had long been resident in this country, and in his early years did valuable scientific work, which he resumed when he retired from his position as partner in the firm of De la Rue and Co. With Dr. Warren de la Rue he devised the chloride of silver-zinc constant battery, and he discovered the value of iodine as a catalyst in chlorination. Of late years he had worked at the Davy-Faraday laboratory of the Royal Institution, and published many articles in the *Journal of the Chemical Society*.

The death of Admiral Sir GEORGE STRONG NARES has robbed the world of a distinguished scientific man who had served his country in more than one capacity. He did valuable geological work in the Arctic Expedition of 1852-1854 under Captain Kellett, and after a period devoted to the training of cadets during which he wrote an excellent book on seamanship, he surveyed Torres Strait, part of the coast of Australia, and the Gulf of Suez. He was a member of the *Challenger* Expedition, but was recalled to take command of a scientific Arctic expedition, which reached 82° 27' N. The geology and biology of Grant Land and Greenland were thoroughly examined by the party, and Captain Nares himself took the astronomical, meteorological, magnetic, and tidal observations. In 1878 Sir George Nares surveyed Magellan's Strait. He was later appointed Professional Officer in the Harbour Department of the Board of Trade and subsequently Conservator of the Mersey.

We have lost in FRANCIS HENRY NEVILLE a metallurgist whose researches were marked by great precision and acumen. In 1888, in conjunction with Mr. C. T. Heycock, he began the investigation of the lowering of the freezing-point of metals by solution in metals, and since that date he had continued his researches on alloys, the most important and complete being those on tin and copper. His mathematical ability and training (he took his degree in the Mathematical Tripos in 1871) were of great assistance to him in his work on the alloys, and he brought a cultured mind and a sound judgment to bear upon the problems which he so successfully solved.

Sir ANDREW NOBLE, whose death occurred on October 22 at the age of eighty-four, possessed an unusual combination of talents, to which his tireless energy enabled him to give full play. His inventive genius first manifested itself in the design and improvement of naval and military guns, and the firm of Armstrong, Whitworth, and Co., Ltd., owed a great debt to his keen business spirit. In 1875, with Professor

Abel, he began his highly important and original work on explosives which has made his name known all over the civilised world. He served on the Council of the Royal Society four times, and was the recipient of the Royal Medal.

Sir ARTHUR WILLIAM RECKER, whose death at the age of sixty-seven occurred on November 1, was a man of conspicuous organising ability and an excellent teacher and lecturer. In 1874 he was chosen as the first Professor of Mathematics and Physics at the Yorkshire College, Leeds, and afterwards occupied the Chair of Physics at the Normal School of Science, South Kensington. In 1901 he was elected Principal of the re-organised University of London, and there performed a difficult task with excellent tact and judgment. He became a Fellow of the Royal Society in 1884, and was one of the Secretaries from 1896 to 1901. He was the recipient of a Royal Medal in 1891. His most important scientific work was connected with terrestrial magnetism, and he took a leading part in the Magnetic Survey of the British Isles, preparing a memoir on the subject for the Bakerian Lecture in 1889.

Dr. WILLIAM JAMES SELL, University Lecturer and Senior Demonstrator in Chemistry at Cambridge, who died in March, was a man of great ability and untiring perseverance, who played a most useful part in the training of students at Cambridge in experimental science. He gave many successful courses of lectures in chemistry, and when opportunity offered he showed that he was capable of successful research, one of his most important pieces of work dealing with the chloro derivatives of pyridine.

Mathematical science has lost one of its most distinguished exponents by the death of Prof. HENRY WILLIAM LLOYD TANNER, to whose educational and administrative talents the University of South Wales and Monmouthshire is deeply indebted. His views on the mathematical training of students were thoroughly sound, and his services to education were by no means limited to his college or university. In addition to his teaching and administrative work at Cardiff, he published many important investigations in mathematics dealing, firstly, with the solution of partial differential equations, and, secondly, with the theory of numbers. These latter researches, which were distinguished by great ingenuity and originality, were not by any means completed when failing powers forced him to resign his professorship and cease work.

Lieutenant-General JAMES FRANCIS TENNANT, Past-President of the Royal Astronomical Society, did valuable work in connection with the Great Trigonometrical Survey of India from 1854 to 1869, and was afterwards responsible for a great number of observations in the total eclipses of 1868 and 1871 and the transit of Venus in 1874. He was most assiduous and enterprising in perfecting methods and collecting data, and the conclusions he drew from his observations were of fundamental importance. For the last twenty years he had done no active scientific work, but he had followed with the keenest interest the developments of astronomy. He died on March 6 at the age of eighty-six.

Three distinguished representatives of our Foreign Members have died since our last anniversary meeting. The name of EMILE HILAIRE AMAGAT is familiar to the physicists of all nations as that of the investigator of the behaviour of gases under pressure, and the brilliant series of researches which he carried through to a successful conclusion showed him to be an experimenter of truly remarkable powers. He determined the compressibility of a number of fluids, and also investigated the effect of pressure upon the freezing-points of liquids. During recent years he had been engaged upon the compilation and arrangement of the numerical data obtained in his experimental work dealing with the specific heat of gases, the internal pressure of fluids, and the corresponding states of matter. Prof. Amagat was elected a Foreign Member of the Royal Society in 1897, and in 1906 he was President of the French Physical Society.

Astronomy has suffered a severe loss by the death of another of our Foreign Members, GEORGE FRIEDRICH JULIUS ARTHUR AUWERS, whose work in connection with the co-ordination of astronomical observations showed him to be a man of extraordinary patience and thoroughness. His chief work was the reduction of Bradley's observations, to which he devoted some ten years of his life, and the preparation of an exhaustive catalogue of stars for the German Astronomical Society. He was a member of many German Astronomical Expeditions, including that for the observation of the transit of Venus in 1874, and he assisted Sir David Gill in observations for the determination of solar parallax at the Cape Observatory in 1889. He was the discoverer of the star "Nova Scorpii," and made many valuable observations of variable stars.

The sudden death of Prof. PAUL EHRLICH in August brought to a close a career of great scientific activity and notable achievements. After graduating in medicine, Ehrlich turned his attention to the affinities of cells for various reagents, and some of the methods and staining agents he employed are still in constant use in biological work. He elaborated a method of standardisation of diphtheria anti-toxin, and was the originator of the side-chain theory of antibodies. His name is probably best known in connection with "606," or Salvarsan, as a cure for Syphilis. He was elected a Fellow of the Royal Society in 1910, and was the Croonian lecturer and the joint recipient with Metchnikoff of the Nobel Prize.

Finally, it is my sad duty to express the regret of the Royal Society at the death of one who, though he had not yet been elected a Fellow, had done work which fully deserved the highest recognition. If his days had been longer he would undoubtedly have ranked amongst our great physicists. On August 10 HENRY GWYN JEFFREYS MOSELEY, Second Lieutenant in the Royal Engineers, died a soldier's death at the Dardanelles. Although only twenty-seven he had published remarkable work. His examination of the X-ray spectra of different elements led to the important discovery that the properties of an element are determined by its atomic number—which marks a notable advance in our knowledge of the structure of the atom. He was instantaneously killed in the execution of his duty. The whole world is the poorer for the tragedy by which he was—

"Gathered to the Kings of Thought
Who waged contention with their time's decay,
And of the past are all that cannot pass away."

The *Copley Medal* has been conferred upon Professor Ivan Petrovitch Pavlov, one of our most distinguished Foreign Members, whose researches in physiology have led to the acquisition of valuable knowledge. By a most ingeniously worked out and original method of making fistulae or openings to the exterior Professor Pavlov has successfully studied the inter-relation of the functions of the alimentary canal. His experiments have shown how the presence of food in one cavity controls the secretion of digestive juices into the next, and he has made many discoveries concerning the conditions which influence the secretory process, while his method has facilitated the study of the chemical changes which occur in the food as it passes through the canal. Moreover, by the method which he calls that of conditioned reflexes, Professor Pavlov has studied from a physiological point of view the influence of the higher brain centres upon the secretion of saliva. He has also investigated the mechanism of the muscle by which bivalves open and close their shells, and the nervous control of the heart, especially through the sympathetic nerves. His resourcefulness and skill have enabled him to make important contributions to Physiological Science, and his work, the true worth of which has, perhaps, not yet been rightly prized, deserves the fullest recognition.

The *Royal Medal*, given annually for physical investigations, has been awarded to Sir Joseph Larmor, whose work in mathematics and physics includes a very wide range

of subjects—Geometry, Dynamics, Optics, Electricity, the Kinetic Theory of Gases, the Theory of Radiation, and Dynamical Astronomy—upon all of which he has published illuminating memoirs. Possibly his chief claim to distinction is the establishment of the theory that radiant energy and intramolecular forces are due to the movements of minute electric charges. This theory is fully worked out in his treatise "Aether and Matter." For a long time Sir Joseph Larmor acted as Secretary to the Royal Society, performing the duties of the office with great success, at the same time continuing with unabated vigour Original Research. The offer of the Royal Medal is a mark of the Society's appreciation and admiration of his invaluable services to Science.

The other *Royal Medal*, for work in the Biological sciences, is this year conferred upon Dr. William Halse Rivers Rivers, whose work in ethnology has contributed largely to the establishment of the subject upon a scientific basis. He was the first to use the genealogical method in ethnological investigations. His remarkable originality combined with sound judgment have enabled him to produce work which will rank with the best that has been done in ethnology.

All chemists will agree that the award of the *Davy Medal* to Professor Paul Sabatier is fully justified. His lengthy researches on the use of finely-divided metals as catalysts are universally known. The hydrogenation of unsaturated organic compounds, especially by means of nickel, has been thoroughly elucidated by Professor Sabatier and his co-worker the Abbé Senderens. The industrial application of the process to the unsaturated acids of the oleic series has already acquired considerable industrial importance. It gives me great pleasure to announce the award, so well earned by Professor Sabatier.

The *Hughes Medal* is awarded to Professor Paul Langevin, who has made valuable contributions to Electrical science, both on the theoretical and experimental sides. He has found by experiment the rate of re-combination and the mobility of ions produced by different processes in gases at various pressures, and he has made an exhaustive study of the theoretical aspects of the inter-diffusion of gases and the mobility of ions.

We meet to-day in circumstances of unparalleled gravity. I am sure we are all deeply conscious of the imperative necessity of modifying the methods of our activities, correcting mistakes, and planning reforms without which we cannot hope to maintain our position among the Nations. England, our England, is passing through a fiery furnace of stress and discipline, and we must face without flinching the bitter lessons to be learned.

The Nation's attitude towards Science is, I think, largely due to the popular idea that Science is a kind of hobby followed by a certain class of people, instead of the materialisation of the desire experienced in various degrees by every thinking person to learn something about innumerable natural phenomena still unsolved; and having learned, to control and apply them intelligently for the benefit of the human race. Many attempts have been made to explain exactly what is meant by Science, and to differentiate true Science from its counterfeit; and it is by no means easy to define it so that the vague general idea of the average man can be replaced by clear and precise conception. Even the most patient investigator, the most acute observer, must constantly feel "Oh, what a dusty answer gets the soul when hot for certainties in this our life." If we refer to our Charter, we shall find that the aim of the Royal Society is promoting Natural Knowledge by Experiments, and if we regard Science as synonymous with Natural Philosophy we may describe it as knowledge relating to natural objects and phenomena connected therewith based upon experiments. Life has been defined as the Act of Correspondence with our environment, and Science may equally tersely be defined as the use of Intelligence in effecting that correspondence.

I believe that the "Hobby" attitude is due to our national

character, and can only be rectified slowly step by step. We cannot suddenly become a truly Scientific nation, either now during the War, or immediately on its conclusion. We shall have to make many fundamental alterations in our ideas and almost to change our natures before such a change can be effected. First among our defects must surely be placed mental inertia, our reluctance to do our thinking for ourselves and the slowness of our intellectual apprehension. This condition is fundamentally different from docility of mind, and its results are more disastrous because it tends to inhibit action on the part of those who should be leaders. Associated with it of course is our inherent stolid conservatism, which makes us too readily satisfied to continue in the ways of our forefathers - ways which, though good enough once upon a time are now obsolete and undesirable. We are sometimes prone to underestimate our opponents' abilities and powers, and usually we have a hearty contempt for outside criticisms of our methods. Our mental inertia makes us slow to put our latent organising power into action.

The problem before us is twofold. We have, firstly, to find out how best to organise all our present forces and employ the material at our disposal to win victory. Many suggestions have recently been made as to the best way to mobilise Science and Invention, so that, for example, Schemes that show some likelihood of having military or naval value can be put at once to the test. At the beginning of the War the Royal Society appointed Committees for this purpose. Their scope could be extended usefully. They include men of Naval and Military experience, whose practical skill and knowledge supplement the theories of men of Science. The second part of the problem is closely interwoven with the first, and its importance to the Nation is hardly inferior. If we neglect to alter our ways, if we continue to disregard the value of scientific work and are content with ignorance of scientific methods on the part of the Authorities, we shall assuredly suffer total defeat in the Industrial war which must of necessity follow upon the conflict of Arms now raging. This is a matter in which men of Science have a great responsibility to the Nation. We must not cease to bring to the notice of the public the facts of which we are too fully aware. The attitude of the Government and the Public towards Science has been mistaken. For this formidable error we suffer and, I fear, must long continue to suffer. The remedy involves many sacrifices and heavy expenditure, probably at first without apparent return. It is to the New Generation now being educated that we must look for betterment of our position; and it is for Youth we must now make plans. We must make all education more Scientific. It is admitted we have much to learn from our adversaries; we must bring Scientific methods to the front. As a well known writer has said of our young generation, "We must not let their Schooling interfere with their Education." I am, however, glad to note that already there are signs on the part of some of our larger Companies and more intelligent Manufacturers of a disposition to remedy shortcomings. The numerous "Polytechnics" that spring up in every manufacturing town (some wonderfully well equipped and organised) are turning out men with at least an insight into the scientific principles that underlie their particular spheres of work, and such men find their services readily accepted. There are also within my knowledge many instances where Manufacturers encourage their lads to attend these Institutions, giving them the necessary time and opportunity. But so far this is the isolated action of a few individuals, and needs both encouragement and organisation.

Should not Science be represented on the Privy Council? It is astonishing that in so august a body Science is almost ignored. Ought we not to have in the Cabinet a Minister of Science with a Board of Advisors similar to that of Agriculture, with the proviso that the Minister of Science should hold his Office primarily by virtue of his Scientific capacity? Power of organisation and general business ability should be regarded as essential secondary qualifica-

tions. The newly appointed Science Councils and Committees might be incorporated under the Ministry of Science—then and then only pure Research would begin to take its place as an invaluable Profession, with a status of its own at least on a level with that of other learned Professions. The leaders of its rank and file would be doing work of fully as much value to the Nation as the work of the Officers of our Naval and Military forces. Then, I feel convinced, the next generation would see the disappearance of listless co-operation between manufacturer and scientific workmen, and we should hear less of the inferiority of British Science as compared with that of our Opponents. Given equal opportunities, our men would speedily give proof of fertility of ideas, of organising powers, and of resource and initiative. Research could be so thoroughly well organised that suitable workers would be jointly engaged with those problems for the speedy elucidation of which there is the greatest need, and the results of their investigations would be at the disposal of all British manufacturers. It rests with us to keep these ideas before the mind of the Public now that at last it is ripe to consider them. "Be wise to-day; 'tis madness to defer."

And now I must pass on to my latest task—perhaps the most fateful of all the tasks I have ever undertaken. I bid a sincere regretful farewell to my Official Colleagues of the Royal Society, whose unfailing and courteous help in my discharge of the duties of the Presidential Office I gratefully acknowledge. I deeply appreciate the honour conferred on me during the last two years, and if I may utilise "an Intelligent Appreciation of Events before they Occur" I heartily congratulate the Society on its election of my Successor. We all know, and the World knows, the lofty place held by Sir Joseph J. Thomson in the august realms of Science—and we all must feel that our Society could not have selected a more suitable and distinguished President.

Ordinary Meeting, November 25, 1915.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"*The Measurement of the Rate of Heat Loss at Body Temperature by Convection, Radiation, and Evaporation.*" By M. FLACK, O.W. GRIFFITH, and L. HILL, F.R.S.

An investigation of the rate of cooling of a surface at body temperature (t) dry (2) wet, under varying conditions of atmosphere, with the view of elucidating the effects of climate, and of heating and ventilation of rooms on health and comfort. A large bulb spirit thermometer is employed of standard pattern—the Kata thermometer; methods of calibrating have been worked out and a factor determined for each, so that the rate of cooling can be expressed in milli-calories per sq. cm. per second. Some thousands of observations have been made in still air under varying conditions, and the cooling curves plotted; the theory of cooling detailed is the work of the late O. W. Griffith. Experimental results, independently obtained, agree with theory. The graph connecting the rate of total heat loss in still air, and the excess of body temperature above that of the enclosure (θ) is a straight line, the equation of which is $H = 0.27 \theta$. The factor (k) of each "kata" can be obtained by determining in still air the rate of cooling at body temperature and the temperature of the air in the enclosure t . If the time be ϕ seconds, then $k = 0.27 (36.5 - t) \phi$. For cooling in still air the equation is deduced $H = 0.0644 (1 + 0.002t) . 05/4$. The cooling of the dry "kata" in still air is found to be independent of the moisture of the air, and to be sensitive to pressure changes of 3 cm. from normal.

From the difference between readings of dry and wet bulb the cooling by evaporation is deduced. This is found to vary with the absolute humidity. The latter can be de-

duced from the readings of the "kata" taken in still air. A table has been constructed for determining humidity from the formula worked out and confirmed by experiment—

$$f = 45.6 - 6.639 E$$

(f = vapour pressure of air, E = rate of evaporative loss).

Cooling by radiation has been studied in an evacuated quartz or glass chamber. At ordinary room temperature and in still air it is estimated the cooling is as much by radiation as by convection. The cooling effect of wind of known velocity, up to 200 miles per hour, has been determined. The graphs of the equation $H \theta = 0.27 + 0.36 \sqrt{v}$ are coincident with velocities up to 35 miles per hour. The curve becomes flattened at higher velocities.

The "kata" is an anemometer sensitive to every eddy as well as to uni-directional wind. The effect of wind on evaporation has also been measured, and the complete equation marked out for the wet "kata" for the range of velocities studied. The acceleration of evaporative cooling is very great during the first ten miles per hour, diminishing gradually to zero value at high-wind velocities.

The balance between air temperature, vapour pressure, and velocity is such that each may be varied within certain limits and still keep the rate of loss of heat—on which our sense of comfort depends—the same. A figure is constructed in which the curves show how this may be brought about.

"The Growth of the Body in Man. The Relationship between the Body-Weight and the Body-Length (Stem-Length)." By E. W. A. WALKER.

Observations have been made on infants, children, and young persons up to early adult age in order to determine whether any definite relationship could be shown to exist between the body-weight and the body-length. By the term body-length is meant the stem-length measured from the top of the head to the line joining the ischial tuberosities. This measurement corresponds to the body-length in animals, and was chosen in order that results obtained for man might be brought into comparison with those for other animals.

The author finds that throughout the period of growth stem-length in man can correctly be expressed as a function of body-weight, and conforms to the formula $l = k \cdot \bar{w}^n$; where l is stem-length, $\bar{w}$ weight, k a constant, and n a power of approximate value one-third. For the male the value of n (to two places of decimals) is 0.33, for the female it is 0.32.

The corresponding values of k (l and $\bar{w}$ being expressed in mm. and grms. respectively) are for grouped males 23.23 and for grouped females 25.60. For the individual boys the average value of k is 23.33, and for the individual girls it is 25.28.

As the body-weight increases the stem-length of the male increases at a somewhat greater rate than that of the female. But the curve represented by the formula for males ($l = 23.23 \bar{w}^{0.33}$) has a point of intersection with the curve represented by the formula for females ($l = 25.60 \bar{w}^{0.32}$).

If the stem-length differ by as much as 16.5 per cent from the value calculated from the body-weight by means of the appropriate formula, the individual may be regarded as abnormal.

"The Rate of Absorption of various Phenolic Solutions by Seeds of Hordeum vulgare, and the Factors governing the Rate of Diffusion of Aqueous Solutions across Semi-permeable Membranes." By Prof. A. J. BROWN, F.R.S., and F. TINKER.

It has been pointed out previously that the seeds of *Hordeum* (barley) are enclosed by a membrane which exhibits the exceptional property of differential permeability. When the dry seeds are immersed in aqueous solutions of most inorganic acids and salts, sugars, &c., water alone passes through their containing membrane; with other

classes of solutes, however, such as the phenols, fatty acids, and monohydric alcohols, the solute enters the seeds together with water. In order to learn something of the physical properties which presumably govern the exhibition of differential permeability (only recognised to a marked extent with living protoplasm and with the coverings of certain seeds), experiments have been made with a series of closely related organic solutes, viz., phenol, catechol, resorcinol, quinol, and pyrogallol, all of which enter the seeds of *Hordeum* when in aqueous solution. The rates of entry of the different solutions into the seeds have been measured and marked differences have been found. A comparison has been instituted between the rates of entry of the phenolic solutions and measures of their leading physical properties. The osmotic pressures, vapour pressures, and viscosities of the solutions exhibit but little variation, and it is evident that these physical properties play no primary part in regulating the rates of entry of the solutions into the seeds. On the other hand, a most intimate inverse relationship between the surface tensions of the solutions and their rates of entry into the seeds has been found.

Experiment appears to justify the conclusion that when the temperatures, osmotic pressures, vapour pressures, and viscosities of a series of solutions of permeable solutes are equal their rates of diffusion across the seed-membrane are inversely proportional to their surface tensions.

"The Controlling Influence of Carbon Dioxide. Part III. The Retarding Effect of Carbon Dioxide on Respiration." By F. KIDD.

Researches previously described led to the conclusion that the resting stage of the moist seed is primarily a phase of auto-narcosis induced by tissue CO_2 . Inhibition of germination by CO_2 was demonstrated in the laboratory and in the field under a wide range of conditions. *Inter alia*, it was shown that the inhibitory value of a given carbon dioxide pressure diminishes with a rise of oxygen pressure and also with a rise of temperature.

These researches have now been carried further, to determine if possible the mechanism CO_2 -narcosis. The present paper deals with the effect of CO_2 upon the respiratory function. The outstanding result shown is that CO_2 causes a marked retardation of respiration. CO_2 narcosis involves a slowing down of the respiratory process. In the course of the experiments described it is first shown that CO_2 depresses the rate of anaerobic CO_2 production. Quantitatively the degree of depression appears proportional to the square root of the concentration over a range from 0 per cent to 50 per cent CO_2 at one atmosphere pressure. It is then shown that the depressant action of CO_2 is equally marked in the case of normal respiration measured either by CO_2 -consumption or CO_2 -production. These results are evidence for a genetic connection between anaerobic and aerobic CO_2 -production in normal respiration, the rate of anaerobic CO_2 -production acting as the limiting factor. When oxygen was supplied in a deficiency, carbon dioxide had then no retarding effect on oxidation. Lastly, it is shown that of the two types of respiration demonstrated by Dr. F. F. Blackman, namely, floating and protoplasmic, it is the former only which is depressed by CO_2 .

NOTICES OF BOOKS.

Coal Distillation, Gasification, and By-products. By J. E. CHRISTOPHER. Wigan: Thomas Wall and Sons, Ltd. 1915.

THIS book is based on two series of articles which have recently appeared in the *Science and Art of Mining*, and which were intended chiefly for mining students. It gives a brief clear account of the manufacture of coal-gas, coke, producer gas, &c., fully illustrated by diagrams of plant. Many statistics of output and cost are included as well as

a great number of analyses. Possibly the most useful part of the book is that devoted to by-products, which gives a short review of the production and properties of the various classes of derivatives.

Brief Course in Metallurgical Analysis. By HENRY ZIEGEL. Easton, Pa.: The Chemical Publishing Co. 1915.

STUDENTS who have had some training in elementary qualitative and quantitative analysis will find that this book provides them with a useful first course in metallurgical work. The products treated include steels and various alloys, rocks, and ores, and usually the author has described only standard methods which are simple and straightforward and are in constant use in analytical laboratories. An exception has been made in favour of electrolytic work with the hydrogen and calomel electrode, which, although it requires some skill in manipulation and also special equipment, gives such satisfactory results that it seems likely to be much used in the future. The directions for all the experimental work seem to be clear and concise, and references are given to larger works for details of more complicated processes. The book is interleaved with blank paper for the student's records of his own work and results.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxi. No. 15, October 11, 1915.

This number contains no chemical matter.

No. 16, October 18, 1915.

Heats of Saturation of some Alkaline Salts.—Albert Colson.—The author has determined the heat disengaged by a molecule of salt passing into a state of saturated solution, keeping the conditions constant so that the numbers obtained are comparable. The salts investigated include potassium nitrate and chloride of ammonium and potassium. As in the case of common salt preliminary determinations of the heat of solution in dilute liquids showed that these quantities vary greatly at about 15°, even when the dilution is much greater than a molecule in 2 litres. The general conclusions to be drawn from the investigation are that the heats of saturation between 5° and 21° vary by at least 7 per cent. The variations are, however, less than those of the heats of solution in the permanent state; i.e., at the moment when they become independent of the dilution at a fixed temperature, and it is a mistake to regard the heats of solution given in thermochemical tables as constants.

Application of Cryoscopy to Chemical Analysis.—Maurice Draper.—The determination of an organic substance in complex mixtures is an exceedingly delicate and very often almost impossible operation, and the author has endeavoured to ascertain how far cryoscopy is adapted to help to surmount the difficulty. His results are encouraging, and it appears that the method may render signal service. If the mixture consists of two substances, A and B, the solution of p grms. of the mixture in P grms. of one of the constituents, A, for example, produces a lowering of the freezing-point which is proportional to the concentration of the mixture in B. The ratio of the lowering observed to that obtained by dissolving p grms. of B in P grms. in A gives at once a first approximation

to the concentration of the mixture in B. If the mixture contains many constituents the weight x of one of them in π grms. of the mixture is given by $x = \frac{MP(k'\Delta - k\Delta')}{100kk'}$,

where M is the molecular weight of the constituent A, P is the weight of the solvent used, Δ and Δ' are the cryoscopic lowerings observed on dissolving π grms. of the mixture in P grms. of any solvent and A respectively, and k and k' are the cryoscopic constants.

MISCELLANEOUS.

Institutions and the War.—Work of the Institute of Metals.—In the cases of certain of the technical institutions the membership figures show no increase since the War, the reason being that these institutions and their members are not particularly associated with war-work. Members, therefore, in such cases, join the fighting forces in large numbers as the best way of serving their country. Though about 10 per cent of the Institute of Metals membership has been temporarily lost in this way most of the members are now assisting the country by working "on munitions." The war activity in the metal industries is such as to tend strongly to reinforce the membership of the Institute, and a ballot for the election of new members has therefore been arranged for December 15. Those wishing to join the Institute should at once write for particulars to Mr. G. Shaw Scott, M.Sc., Secretary, Caxton House, S.W. It is probably due to their desire to see and to study the volumes of the *Journal of the Institute of Metals* that so many new members are joining the Institute of Metals just now. They cannot readily get away to meetings of the Institute in war-time, but they find all the papers that were read at the meetings recorded in the invaluable Transactions, along with much additional information respecting the use and working of the non-ferrous metals and alloys.

British Empire Industrial Exhibition.—An agreement has been concluded between the Institute of Industry (of Great Britain and Ireland), Ltd., and the British Dominions Exhibition, Ltd., whereby the Institute takes over the whole of the latter undertaking and the management of the British Empire Industrial Exhibition, which the British Dominions Exhibition, Ltd., was formed to promote. The Committee desire to make it generally known that they have placed proposals before the various Dominion Governments which provide for the erection of permanent Exhibition buildings within fifteen minutes' walk of the Strand and covering an area of about ten acres, which are likely to be favourably considered. It is the intention to hold in these buildings a comprehensive Exhibition of British Industries within twelve months of the conclusion of peace, and also one of the Natural Resources of the Empire. The Exhibitions will be continued at frequent intervals thereafter.

MEETINGS FOR THE WEEK.

- MONDAY, 13th.—Royal Society of Arts, 4.30. (Cantor Lecture). "Optical Glass," by W. Rosenhain.
— Biochemical Society, 5.30. (At the Lister Institute, Chelsea Gardens, London, S.W.).
WEDNESDAY, 15th.—Royal Society of Arts, 4.30. "Carillons and Carillon Playing" (with Illustrations), by Josef Denyn and W. W. Starmer.
— Microscopical, 8. "Use of Ultra-violet Light in Microscopy," by J. E. Barnard.
THURSDAY, 16th.—Royal Society of Arts, 4.30. "The Indian Jute Industry," by C. C. McLeod.
— Chemical, 8. "Propagation of Flame in Mixtures of Hydrogen and Air—The 'Uniform Movement,'" by W. A. Haward and T. Otagawa.
— "Molecular Volumes of the Hyponitrites of the Alkali Metals and Metals of the Alkaline Earths," by P. C. Ray and R. De.

THE CHEMICAL NEWS.

VOL. CXII., No. 2926.

NOTES ON PLANT CHEMISTRY.

By P. Q. KEEGAN, LL.D.

Hair Moss (Polytrichum commune).—This plant assembles in dense tufts and cushions of deep greenery on heaths, moist woods, and turbaries. Its chemistry is rather tame, and apparently not specially indicative of any specific physiological activity; one reason for which may be that the constituents for the most part are not readily extracted by the ordinary menstrua, or only in such quantity as renders their mode of origin or their functions rather dubious. However, I will now relate the facts of the analysis as follows:—In June the dried moss yielded to boiling benzene 1·1 per cent of an unsaponifiable waxy matter which was tinged by a trace of carotin, and there was no phytosterol. The alcoholic extract contained some more yellow wax and a little chlorophyll, and its aqueous solution was acid and faintly bitter, had traces of a saponin apparently, and responded very clearly to the tests for saccharose. Further treatment of the residue of the plant indicated the presence of nitrate, much pectosic mucilage, and pentosan, a little starch and cellulose hydrate (amyloid, perhaps), and a red-brown resinous matter extractable by dilute soda and soluble in sulphuric acid with a brown colour. There was no dextrine, alkaloid, or oxalate. The ash of the plant in October was about 2·4 per cent, and contained 16·4 per cent soluble salts, 45·8 silica and sand, 7·3 CaO, 3·4 MgO, 12·1 oxide of iron, 4·3 P₂O₅, 3·7 SO₃, with some manganese and traces of chlorine and carbonate. In June the ash contained 41·9 per cent soluble salts and only 16·3 silica. At first sight the above analysis seems rather meagre, but if we carefully observe the habit of the plant, and are aware that the protoplasm of mosses is extremely sensitive to the influence of the contents of the currents of water which traverse their tissues, we must conclude that they are capable of a pretty active power of assimilation. The array of vertical cells on the upper surface of the leaves, when exposed to the air in a moist atmosphere, produce starch, oil, &c., very rapidly and efficiently. Moreover, the humus of the heaths and turbaries where it grows contains colloidal combinations of the diverse constituents of the carbonaceous destruction of plants, and these, being taken up by the rootlets or root hairs and digested there, are absorbed or assimilated by the protoplasm in the form of condensed carbohydrates. As regards the process of deassimilation, it proceeds no further than the formation of a resin which is yellowish, has an acid function, and yields no special reactions. This resin plugs up the intercellular spaces and the stomatic air-cavities in the lower portion of the stem, and thus greatly slackens the physiological activity and modifies the protoplasmic content of the cells situated there, thus clearly showing that this part of the organism is of no further service after the fruiting is accomplished. Although Czapek by long boiling with water or dilute soda under pressure apparently extracted a phenolic and a tannic body from the cell-wall of various mosses, I am not convinced that these bodies exist there as original constituents. After careful examination I am inclined to conclude that the yellow colour given to the cell-wall of mosses by soda and the reactions of same given by FeCl₃ and by Millon's reagent are due to some humin matter sucked up from the soil into the tissues, similarly as certain fungi, according to Neumann, can absorb tannin (0·04 per cent) into their tissues, where it is chemically decomposed. Mosses are very tenacious of life, the term of their existence is in most cases unlimited, every part of them may give rise to protonema; i.e., a rudimentary shoot and thallus, and those species which inhabit moist places emit a great quantity of CO₂. All

these properties seem to be connected with the essentially reproductive character of their cells; i.e., they have a clearly defined nucleus and abundant white translucent alkaline protoplasm, the vacuoles of which have no supply of nutriment, organic or inorganic. The doctrine of evolution has been sharply held up by mosses, no passable bridge having been found between them and the algae on one side and the ferns on the other. Mosses may perhaps be a sort of "reproductive" offset from, say, grasses; but in that case the plant evolution theory would be worse confounded than before.

Early Purple Orchis (O. mascula).—This plant is found in meadows, and in certain parts of woods and pastures where there is no rich supply of food salts. It is a succulent plant of slow growth and very difficult to cultivate artificially, its germination necessarily requiring the concurrence of fungi, which frequently depends on chance. The mycorrhiza exist always inside the cells of the roots (not of the tubers) as pellets of compact filaments (hyphæ), which are sometimes ultimately completely digested by the plant. Hence it would seem, as Gallaud opines, that the supposed symbiotic nature of these mycorrhiza is more like that of a parasite, but their infestation serves to react in a physico-chemical manner upon all the tissues of the plant. On June 20 the dried over-ground parts of the plant yielded to boiling benzene 1·7 per cent of wax, with a very little carotin and some fat oil; the alcoholic extract had a bitter taste, and contained a moderate quantity of flavone giving the reactions of quercitrin, also a large quantity of free glucose, and some resin and bitter principle which gave no green coloration when warmed with nitric acid. There was no nitrate, tannin, alkaloid, or starch, but much pectosic mucilage and a little pentosan; also a considerable amount of oxalate of calcium reprecipitating in fine crystals after extraction; the crude fibre amounted to 40 per cent of the dried material. The ash of above was 6·5 per cent, and contained 47·3 per cent soluble salts, 5·2 silica, 20·5 CaO, 3·8 MgO, 7·8 P₂O₅, 3·8 SO₃, and 7·8 Cl; there was much soluble carbonate, and about 3 per cent oxides of iron and manganese. The tubers when young contain starch, sucrose, volatile oils, and mannin, but no inulin, as reserve substances which are mostly used up at flowering time, when a new tuber is immediately produced and rapidly forms similar reserves as before. The floral organs of orchids have commanded much attention for many years; in the plant under review the corolla is of a rich purple colour, though there is no tannin in any of the organs; the conditions, viz., the lanceolate leaves rarely rising far from the ground, and the long bare stem are exactly those which specially favour the development of anthocyanic pigment in the corolla. Blue flowers are said to occur in three genera of Orchidaceæ, but the presence of quercitrin or quercetin in the order induces me to conclude that these are not true blues. I have noticed that this orchid does not grow on specially damp peaty places, so that the fact as shown by the above analysis that it contains no starch and little pentosan is readily explained. The most remarkable fact is the presence of free aldehydic sugar, and a portion of a gathering got in June being left in a closed drawer for five months was found to still retain a large amount of the same reducing substance. "Succulent plants," says André, "possess a kind of very special vegetation which is revealed by their tenure of organic acids and by remarkable peculiarities as to what concerns the variations in the soluble amides and the ternary matters." The protoplasm of succulent plants has special properties, and the high percentage of water favours and prolongs the phenomena of the dissolving power of the diastases on the starch, &c. Such would seem to be the prevalent view of cases like this one; but the meadow land rich in humus formed from the debris of certain plants seems to accumulate carbon in a special manner, which, being absorbed by the roots and tubers of the orchid, are digested there, and when the transpiration is strong, as in the fleshy leaves of some tropical orchids,

copious starch is formed thereby; whereas when the transpiration is feeble soluble carbohydrates are alone produced. According to Van Tieghem the tuber of the orchid under review is composed of a number of separate roots which have a common growth, and all constitute together a single tuber, and hence it is really a tuberous root; if it were not so it would be difficult to explain the presence therein of some of its chemical constituents. It is admitted that carbonaceous matter may be absorbed by the roots of plants, but the amount of it thus taken up is too small to be worth considering. I do not agree with this opinion. I am firmly convinced that it is impossible to explain the very large amount of starch and mucilages contained in the stem and leaves of various marsh and water plants which I have analysed, if it be contended that these carbohydrates are originally produced only and solely by the action of the leaves or other organs evolving chlorophyll. According to Griffon the non-green species of *Orchis*, such as *Neottia*, which is all pale reddish brown, are capable owing to their mycorrhiza of extracting their carbon from humus matters. On the other hand, André in 1912 declared that "the carbon nutrition of the plant at the expense of the humic matter of the soil has not yet been proved." Nevertheless, I think that if a certain number of marsh plants were examined the standard of proof as respects this question will be raised very high.

Marsh Marigold (Caltha palustris).—This plant flourishes most effectively on valley bottoms of black muddy soil on stream-edges, or often partly submerged. It belongs to the hellebore tribe of the much discussed order Ranunculaceæ, which according to some systematists ranks amongst the highest Angiosperms, while others regard them as merely Monocotyledons. On May 15 the dried leaf blades extracted boiling benzene yielded 1.6 per cent of much carotin, with some wax and a little fat-oil. The alcoholic extract contained much flavone, which was a mixture of iso-rhamnetin with a little quercetin. There was also an acid resinous glucoside (helleborin) like a saponin, and about 2 per cent caffein. Further treatment showed the presence of sucrose, a large quantity of mucilage (secreted by glands in the teeth, the sheaths, and the nerve-grooves of the leaf), also pentosans, somnitate, but no reserve starch or oxalate of calcium. Warm dilute HCl extracted a small quantity of an alkaloid which seems to be veratrine, as it gave a bluish reaction with H_2SO_4 and sugar. There was 9.7 per cent of ash, which contained 43.5 per cent soluble salts, 6.5 silica, 19.1 CaO, 4 MgO, 5.5 P_2O_5 , 5.3 SO_3 , and 8.7 Cl, with only a little iron and manganese and no soluble carbonate. The special feature of this analysis is the presence of caffein along with quercetin, which latter, however, may not be actually present as such in the plant, but only split off during the analysis from the iso-rhamnetin; the presence of copious mucilage is incidental to the root action already specified. The floral organs yielded 2.6 per cent of carotin and wax; they had also iso-rhamnetin, but no quercetin or tannin; also very much mucilage, but no starch; the ash yielded 55.2 per cent soluble salts, 5.3 silica, 9.2 CaO, 6.2 MgO, 10.9 P_2O_5 , 7.1 SO_3 , and 5.5 Cl; there was much soluble carbonate and a little manganese. It must be noted that the floral envelopes are formed of sepals and not of petals, and are therefore of a vigorous anatomical structure, have stomata, and their protoplasm is capable of differentiation with production of chromoplasts which by a process of assimilation evolve starch, fat-oil, protein crystals, chlorophyll, and the carotin, which aided by the shimmer of the oil impart a brilliant golden, almost fiery, aspect to these organs. The root is of the hydrophilic type and has long, cylindrical, unbranched side-roots; it contains starch, but was not further examined. The black mud in which it grows is supposed to be brought about by the action of moulds (not bacteria), which only grow in a neutral medium and are said to take part in the mineralisation of organic nitrogen; they reabsorb the ammonia and produce new amido-nitrogenous substances. The analysis of the Marsh

Marigold is specially interesting, inasmuch as it enables us to propound three important results of a general nature, viz.:—1. The production of mucilage is in no way related to the production of oxalate of calcium. 2. The absorption of humic matter from the soil serves apparently as a basis for the formation of mucilages and hemicelluloses, but not of starch and certain sugars. 3. It would seem that plants which bear flowers tintured by carotin require, even when the top soil is peaty, a substratum of sand or gravel where the relation of nitrogen to carbon is rather high, i.e., where abundant soil nitrogen is readily available, and may be easily absorbed by the roots. Most yellow-flowered plants seem to grow on dry calcareous or non-peaty soils, as in the famous "Sunflower State" of Kansas, U.S.A. On the whole I am inclined to conclude that Ranunculaceæ, although structurally comparable to Monocotyledons, are chemically superior thereto.

Some Woodland Phenomena.—Of all our native trees the Alder is perhaps the most difficult to analyse satisfactorily. One special reaction may be noticed. The bark of a twig cut in March was boiled in water, and on adding to the filtered cold solution one drop of hypochlorite of sodium solution a deep indigo-blue coloration was immediately produced, which vanished almost at once; this was repeated two or three times with a similar result, but finally no blue was observed. So far as my experience of plant extracts has gone this reaction is absolutely unique. It was not given by the tannin alone, or by the emodin alone which occur in this bark. It would appear according to my examination that alder tannin does not contain a phloroglucol nucleus, and also that its phlobaphene is easily alterable, so that the emodin is probably formed by its oxidation with loss of water and destruction of the phloroglucol nucleus.

By kind permission I was enabled to examine the leaves of a beautiful British grown specimen of the mammoth tree of California (*Sequoia gigantea*). Without going into detail I may mention that the waxy and resinous constituents of these leaves gave no special reactions; there was little carotin, but much phytosterol. There was a little tannoid, probably fisetin. The tannin was powerfully reductive, and gave the usual reactions of a catechol very decisively, and although it precipitated tartar emetic at once, gave a bluish solution with Fe powder, and faintly greenish precipitates with baryta water and with Millon's reagent, it yielded no gallic acid when boiled with dilute acids. It yielded a specially beautiful phlobaphene, indicating the absence of "humic" in the extracts, or of any decomposition of tannin in the leaves, and this in fact seems to be characteristic of all the Coniferæ that I have examined, which means that these tannins are very stable, and are free from carbohydrate contamination owing to a particular construction of the vascular system of the trees. The leaves also contained much gum, and much sucrose, or a glucoside yielding it. After steeping in cold benzene or cold alcohol, drying, and then boiling in water, a large quantity of starch was extracted. There was also much pectosic mucilage, and the reactions of pentosans were very pronounced. There was no alkaloid or oxalate of calcium. According to Heyl the tannin of this *Sequoia* cone yields phlobaphene, and some gallic acid and sugar when boiled with dilute sulphuric acid; this is probably correct, as the tannins of fruits seem generally more readily oxidisable than those of leaves, or sometimes even of barks.

Patterdale, Westmorland.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 6th inst., the Duke of Northumberland, K.G., President, in the Chair. The Honorary Secretary announced the decease of Sir Arthur Rucker, M.A., LL.D., D.Sc., F.R.S., and Prof. Raphael Meldola, LL.D., D.Sc., F.R.S., F.R.A.S., F.C.S., F.I.C., Members of the Royal Institution, and Resolutions of Condolence with the relatives were passed.

THE CONDUCTIVITY AND VISCOSITY OF SOLUTIONS OF ELECTROLYTES IN FORMAMID.*

By P. B. DAVIS, W. S. PUTNAM, and HARRY C. JONES.

(Continued from p. 285).

Purification of the Solvent.

It might be well to note at the outset that neither a clean melting-point nor a constant boiling-point is a sufficient criterion for the purity of the solvent for conductivity purposes; since it has been found by ourselves and others that a constant boiling liquid such as formamid may be separated into fractions of widely different specific conductivities. That this is true is due, no doubt, in this particular case to the fact that minute quantities of the products of hydrolysis, such as would have no measurable effect on the apparent boiling-point of the liquid, on account of the high dissociating power of the formamid, produce a marked increase in its conductivity.

The chief criterion therefore in judging of the purity of the solvent used in this investigation was its specific conductivity. The material with which we started was obtained from Kahlbaum, and had a specific conductivity of about 67.4×10^{-5} , or about that of tap-water. Samples obtained from Bender and Hobein, Schuchardt, and from Hoffman and Kropff proved, from the conductivity standpoint, to be little or no better than the above.

As has already been pointed out, formamid is hygroscopic, forms a true solution with water, and subsequently undergoes slow hydrolysis into ammonium formate. The first problem therefore that presented itself, was the removal of any dissolved water not already acted on; and, second, the removal of the products of hydrolysis already present. The method of purification finally adopted made it necessary to design and construct suitable apparatus for distillation in comparatively high vacua.

A third problem presented itself in connection with the preservation and subsequent manipulation of the solvent and of solutions in it, in such a manner as to incur minimum exposure to moisture. In addition, the expense of the solvent made necessary the recovery of it with the least possible loss by decomposition from solutions of salts in this solvent.

The removal of dissolved water was finally effected by the use of carefully dehydrated sodium sulphate. After testing a number of other dehydrating agents, such as magnesium sulphate, calcium chloride, sulphuric acid *in vacuo*, &c., it was found that sodium sulphate produced a smaller loss of materials from combination with it than any of the other dehydrating agents studied.

Formamid was therefore allowed to stand for several weeks over anhydrous sodium sulphate in carefully sealed glass stoppered bottles placed in a cool dark room. An attempt was made to effect a preliminary purification of formamid by fractional crystallisation, but the end product, after several fractionations, invariably showed a higher conductivity than the original substance. We were therefore forced to conclude, as were Freer and Sherman (*Am. Chem. Journ.*, 1898, xx., 223) in preparing formamid, to study its sodium salts, that a properly conducted distillation process was the best one available.

As a rule, starting with Kahlbaum's so-called chemically pure formamid, from three to four distillations yielded a product sufficiently pure for our purpose. The decrease in the conductivity with successive distillation is shown in Table A.

While the end fraction in this case was sufficiently pure for use, a fourth distillation yielded a product with the conductivity of about 3.4×10^{-5} ; although the exact minimum conductivity of this solvent has thus far not been ascertained, we have obtained small lots with a specific conductivity of 2.8×10^{-6} , or from two to three times the

value for the conductivity water used in this laboratory. Walden used in his work a product with a conductivity of 7.5×10^{-4} , but obtained a small fraction of about 10 per cent of the original material, with a conductivity of 4.7×10^{-5} . Our solvent was from 35 to 40 per cent of the original volume with a maximum specific conductivity of 4.8×10^{-5} , with a minimum of 1.37×10^{-5} and an average of 2.7×10^{-5} .

TABLE A.—Specific Conductivity.

Original material	67.4 $\times 10^{-5}$
First distillation .. {	First fraction 78.5 $\times 10^{-5}$
	Second fraction 43.5 $\times 10^{-5}$
	Third fraction 112.3 $\times 10^{-4}$
Second distillation . {	First fraction 204.2 $\times 10^{-5}$
	Second fraction 153.8 $\times 10^{-5}$
	Third fraction 67.4 $\times 10^{-5}$
Third distillation—First fraction	{ 24.6 $\times 10^{-5}$
	{ 10.3 $\times 10^{-5}$
	{ 4.8 $\times 10^{-5}$

Salts.

On account of the instability of the solvent formamid in the presence of moisture, the salts used in this investigation were all dehydrated with special care at the highest temperature which it was possible to use for these substances.

Solutions.

The more concentrated solutions in formamid were made up by direct weighing; the more dilute by diluting the more concentrated. This operation was much facilitated by the use of two burettes holding 50 and 10 cm. respectively; the one being employed for the solvent, the other for the one-tenth normal solution. Each burette was connected with the reservoir containing the solvent or the solution by a syphon provided with a glass stopcock, and access of moisture being prevented by calcium chloride tubes connected with both the burettes and the reservoirs.

The solvent was kept until required in half-litre glass stoppered Erlenmeyer flasks, and the solutions when made up were preserved in 35 cc. flasks of similar design, which were sealed with rubber cement.

On account of the high price of the solvent, only 25 cc. of each solution was prepared; this amount serving both for conductivity and viscosity measurements. All operations in preparing the solutions were carried out at 20°.

Conductivity Apparatus.

The conductivity apparatus used in this investigation was identical with that employed in our earlier work on binary and ternary mixtures of water, acetone, and glycerol; the method of obtaining duplicate readings and other details being exactly the same as in the earlier work, with the exception of the use of a rocking commutator with mercury contact, instead of the two-blade double-throw switch used in reading both ends of the bridge; the object being to eliminate as nearly as possible all external resistance.

The conductivity cells were also of the type recently employed in this laboratory for work with non-aqueous solvents, and were carefully standardised at regular intervals.

Viscosity Apparatus.

The apparatus used in this work was essentially the same as in our earlier investigations. We have designed and used an improved support for the viscometers, which is particularly well adapted to our new thermostat. A new pycnometer has also been devised, which has proved to have advantages over the older form. (For a complete description of all apparatus see Carnegie Institution of Washington, Publications Nos. 210 and 230).

Both conductivity and viscosity measurements were

* From the *Journal of the Franklin Institute*, November, 1915.

made at 15°, 25°, and 35°; the data are tabulated in the usual manner, tables of constants and the use of a calculating machine greatly facilitating the calculations.

TABLE II.—Comparison of the various Solvents.

Solvent.	Dielectric constant.	Association factor.	Viscosity at 25°.
HCN	95		
HCONH ₂	94	6.18	0.0326
H ₂ O	81.7	3.81	0.0089
CH ₃ OH	32.5	3.43	0.0056
C ₂ H ₅ OH	21.7	2.74	0.0111
C ₃ H ₇ (OH) ₃ ..	16.5	1.80	5.854
CH ₃ -CO-CH ₃ ..	20.7	1.26	0.0035

TABLE III.—Sodium Bromide in Formamid.

V.	Molecular conductivity.			Dissociation.		
	15°	25°	35°	15°	25°	35°
2	11.83	15.53	19.76	62.1	63.1	63.4
4	13.80	18.01	22.82	72.4	73.2	73.6
10	16.20	21.09	26.64	85.0	85.7	86.0
50	17.46	22.62	28.55	91.6	91.9	92.1
200	18.79	24.36	30.59	98.6	98.9	98.7
400	19.06	24.62	30.99	100.0	100.0	100.0
K	1.53 × 10 ⁻⁵ 1.99 × 10 ⁻⁵ 2.46 × 10 ⁻⁵					

(K is the specific conductivity of the solvent).

Viscosity and Fluidity.

V.	η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°
2	0.05578	0.04081	0.03120	17.93	24.50	32.05
4	0.04883	0.03678	0.02837	20.48	27.19	35.25
10	0.04523	0.03413	0.02666	22.11	29.30	37.51
Solv.	0.04274	0.03194	0.02511	23.40	31.31	39.83

TABLE IV.—Sodium Iodide in Formamid.

V.	Molecular conductivity.			Dissociation.		
	15°	25°	35°	15°	25°	35°
2	11.92	15.71	20.01	64.7	65.6	66.1
4	14.17	18.57	23.59	76.9	77.5	78.0
10	15.91	20.67	26.05	86.3	86.3	86.1
50	17.17	22.33	28.17	93.2	93.2	93.1
200	18.27	23.80	29.98	99.1	99.3	99.1
400	18.43	23.96	30.25	100.0	100.0	100.0
K	2.23 × 10 ⁻⁵ 2.83 × 10 ⁻⁵ 3.48 × 10 ⁻⁵					

Viscosity and Fluidity.

V.	η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°
2	0.05425	0.03997	0.03065	18.43	25.02	32.63
4	0.04822	0.03640	0.02800	20.74	27.47	35.71
10	0.04532	0.03381	0.02653	22.07	29.58	37.69
Solv.	0.04307	0.03302	0.02570	23.22	30.29	38.91

TABLE V.—Sodium Chromate in Formamid.

V.	Molecular conductivity.		
	15°	25°	35°
10	24.57	33.66	42.66
50	31.46	34.48	52.18
200	34.34	44.82	56.38
400	39.00	50.79	—
800	42.64	55.07	69.16
1600	72.06	93.51	116.44
K	1.30 × 10 ⁻⁵ 1.65 × 10 ⁻⁵ 2.03 × 10 ⁻⁵		

Viscosity and Fluidity.

V.	η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°
10	0.04966	0.03633	20.14	27.30		
Solv.	0.04301	0.03221	23.25	31.05		

TABLE VI.—Potassium Chloride in Formamid.

V.	Molecular conductivity.			Dissociation.		
	15°	25°	35°	15°	25°	35°
2	14.12	18.25	22.94	67.9	68.3	68.7
4	16.15	20.84	26.13	77.6	78.0	78.2
10	18.06	23.27	28.99	86.8	87.1	86.8
50	19.27	24.94	31.12	92.6	93.3	93.2
200	20.66	26.60	33.10	99.3	99.5	99.1
400	20.80	26.73	33.39	100.0	100.0	100.0
K	2.94 × 10 ⁻⁵ 3.75 × 10 ⁻⁵ 4.69 × 10 ⁻⁵					

Viscosity and Fluidity.

V.	η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°
2	0.05251	0.03922	0.03000	19.04	25.50	33.33
4	0.04724	0.03572	0.02794	21.17	28.00	35.79
10	0.04457	0.03386	0.02642	21.94	29.53	37.85
Solv.	0.04304	0.03256	0.02542	23.23	30.71	39.34

TABLE VII.—Potassium Iodide in Formamid.

V.	Molecular conductivity.			Dissociation.		
	15°	25°	35°	15°	25°	35°
2	14.42	18.67	23.29	70.7	71.0	71.0
4	16.32	21.05	26.34	80.0	80.1	80.3
10	18.23	23.45	29.21	89.4	89.2	89.0
50	19.25	24.87	31.03	94.4	94.6	94.5
200	20.39	26.28	32.81	100.0	100.0	100.0
400	20.26	26.29	32.82			
K	2.23 × 10 ⁻⁵ 1.83 × 10 ⁻⁵ 3.48 × 10 ⁻⁵					

Viscosity and Fluidity.

V.	η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°
2	0.04982	0.03710	0.02884	20.07	—	34.67
4	0.04631	0.03525	0.02716	21.59	28.37	36.81
10	0.04418	0.03353	0.02629	22.64	29.82	38.04
Solv.	0.04307	0.03302	0.02570	23.22	30.29	38.91

TABLE VIII.—Potassium Sulphocyanate in Formamid.

V.	Molecular conductivity.			Dissociation.		
	15°	25°	35°	15°	25°	35°
2	15.15	19.10	24.28	70.0	69.2	70.4
4	17.42	22.31	27.87	80.6	80.8	80.6
10	19.04	24.38	30.35	88.0	88.3	88.0
50	20.02	25.61	32.16	92.6	92.8	93.3
200	21.21	27.19	33.89	98.1	98.5	98.3
400	21.62	27.60	34.47	100.0	100.0	100.0
K	1.07 × 10 ⁻⁵ 1.37 × 10 ⁻⁵ 1.69 × 10 ⁻⁵					

Viscosity and Fluidity.

V.	η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°
2	0.04891	0.03657	0.02838	20.45	27.35	35.24
4	0.04585	0.03473	0.02713	21.81	28.79	36.86
10	0.04369	0.03280	0.02574	22.89	30.49	38.85
Solv.	0.04294	0.03258	0.02554	23.29	30.69	39.15

(To be continued).

Change of Address.—On and after December 25 next our address will be 6, Earl Street, Westminster, S.W. where we have secured larger and more commodious laboratories. After having been established here some thirty-five years we were naturally extremely loth to change our address, but our lease having expired and the owner having sold the building for demolition, there was unfortunately no alternative.—HENRY FAJFA & Co. (D. B. Butler, Principal), Portland Cement Testing Works and Chemical Laboratories, 41, Old Queen Street, Westminster.

RADIOMETRIC MEASUREMENTS OF THE IONISATION CONSTANTS OF INDICATORS.*

(SECOND COMMUNICATION).

By M. G. PAULUS, J. F. HUTCHINSON, and HARRY C. JONES.

(Concluded from p. 283).

Results with Rosolic Acid.—For the first determination of the indicator constant K_i , solutions were used containing in 100 cc., 50 cc. rosolic acid, 25 cc. Na_2HPO_4 , and 5, 10, and 15 cc. HCl respectively.

These solutions were prepared from the stock solutions, and solutions were allowed to stand for twenty-four hours, which time, according to the results of the preliminary work, was amply sufficient for equilibrium to be established. In Table IV. are given the percentage transmissions for a depth equal to 20 mm. of each of these solutions, the values being in every case the average of two measurements. These are the values to be substituted for (I/I_0) in Equation 6. As has previously been explained, the ratio c/c_1 also depends upon the percentage transmission $(I/I_0)'$ of an indicator solution completely transformed into the red component, and also upon the percentage transmission $(I/I_0)'$ of an indicator solution completely transformed into the yellow constituent. The transmissions $(I/I_0)'$ used are the averages of those recorded in Columns 2, 3, and 4, Table II. It was found that solutions containing 50 cc. of the stock solution of the indicator, plus the necessary amount of hydrochloric acid to convert the indicator entirely into the yellow component, were completely transparent to the five wave-lengths of light used. The transmissions $(I/I_0)'$ are therefore in every case 100 per cent.

In Table IV. the ratios $c/c_1 = (In)/(HIn)$ were calculated from Equation 6, and the constants K_i from Equation 1. The hydrogen ion concentrations were calculated by means of Equation 7, α_1 and α_2 being interpolated from the percentage ionisations of monosodium and disodium phosphates at various dilutions given by Abbot and Bray (*Journ. Am. Chem. Soc.*, 1909, *xxxi.*, 729).

Another series of solutions, similar to the preceding with the amounts of acid indicated in Table V., were prepared, and allowed to stand sixteen hours, in which time all of them had come to equilibrium. The percentage transmissions (the average values of two determinations are given), calculated ratios c/c_1 , and the constants K_i , are given in Table V. The same values for $(I/I_0)'$ and $(I/I_0)''$ were used as for the preceding determination.

The values of K_i , Table V., show a steady decrease from 5.65×10^{-8} to 2.89×10^{-8} , as the solution becomes less alkaline. The average constant is 3.91×10^{-8} . (The value given by Salm, *Zett. Phys. Chem.*, 1907, *lvii.*, 496, is 1.1×10^{-8}). It is to be remembered that the constants were determined on the assumption that rosolic acid is monobasic. As is well known the indicator is dibasic, and the decrease in the constants with decreasing alkalinity was expected. Rosolic acid actually dissociates in two

stages according to the equations, $\text{H}_2\text{In} = \text{HIn} + \text{H}^+$, and $\text{HIn} = \text{In}^- + \text{H}^+$.

Behaviour of Rosolic Acid as a Dibasic Acid.—With regard to the two ions HIn^- and In^{2-} , three assumptions can be made:—(1) That the intermediate ion HIn^- is yellow and the secondary ion In^{2-} is red; (2) that the ion HIn^- is red and the ion In^{2-} is yellow; (3) that both the ions HIn^- and In^{2-} are red. In the first case the ratio of the red to the yellow component will be given by—

$$c/c_1 = \frac{\text{In}^{2-}}{\text{HIn}^- + \text{H}_2\text{In}} \quad \dots \quad (9).$$

TABLE IV.
 $\lambda = \text{A.U.}$ $\text{H}^+ \times 10^8$ Average percentage transmissions. c/c_1 $K_i \times 10^8$.

Solution No. 1.—(5 cc. HCl) (25 cc. Na_2HPO_4).

5598		26.4	0.803	3.60
5648		36.6	0.811	3.64
5698	4.484	49.6	0.734	3.20
5748		59.8	0.920	4.13
5798		70.6	0.937	4.20

Solution No. 2.—(10 cc. HCl) (25 cc. Na_2HPO_4).

5598		49.0	0.306	3.23
5648		59.4	0.302	3.19
5698	10.53	70.6	0.266	2.81
5748		76.8	0.326	3.44
5798		83.7	0.329	3.48

Solution No. 3.—(15 cc. HCl) (25 cc. Na_2HPO_4).

5598		67.5	0.148	2.89
5648		76.4	0.136	2.66
5698	19.52	80.2	0.154	3.05
5748		85.5	0.171	3.34
5798		87.7	0.223	4.35

TABLE V.

Solution No. 1.—(3 cc. HCl) (25 cc. Na_2HPO_4).

5598		12.1	2.28	5.77
5648		20.8	2.33	5.89
5698	2.533	32.0	2.20	5.56
5748		48.1	2.14	5.42
5798		60.9	2.22	5.63

Solution No. 2.—(5 cc. HCl) (25 cc. Na_2HPO_4).

5598		25.4	0.822	3.69
5648		35.7	0.847	3.81
5698	4.484	48.3	0.785	3.53
5748		60.8	0.849	3.82
5798		71.0	0.906	4.07

Solution No. 3.—(10 cc. HCl) (25 cc. Na_2HPO_4).

5598		50.7	0.288	3.03
5648		59.7	0.298	3.14
5698	10.53	68.7	0.293	3.08
5748		78.1	0.298	3.14
5798		84.2	0.314	3.30

Solution No. 4.—(15 cc. HCl) (25 cc. Na_2HPO_4).

5598		67.6	0.148	2.89
5648		74.6	0.150	2.93
5698	19.52	80.8	0.146	2.89
5748		87.2	0.146	2.85
5798		90.2	0.167	3.26

In addition, the equilibrium equations given below have to be considered.—

$$\frac{(\text{H}^+)(\text{HIn}^-)}{(\text{H}_2\text{In})} = K_1 \quad \frac{(\text{H}^+)(\text{In}^{2-})}{(\text{HIn}^-)} = K_2 \quad \dots \quad (10).$$

By combining these three equations we obtain—

$$c/c_1 = \frac{K_1 K_2}{\text{H}^+ (\text{H}^+ + K_1)} \quad \dots \quad (11).$$

In the second case, when the ion HIn^- is red and the ion In^{2-} is yellow, the ratio becomes—

$$c/c_1 = \frac{\text{HIn}^-}{\text{H}_2\text{In} + \text{In}^{2-}} \quad \dots \quad (12),$$

and from Equation 10—

$$c/c_1 = \frac{\text{H}^+ + K_1}{\text{H}^2 + K_1 K_2} \quad \dots \quad (13).$$

* From the *Journal of the American Chemical Society*, xxxvii., No. 7.

In the third case, *i.e.*, when both ions HIn^- and $\text{In}^{=}$ are red, the ratio is given by—

$$c/c_1 = \frac{\text{HIn}^- + \text{In}^{=}}{\text{H}_2\text{In}} \quad \dots \quad (14),$$

whence,—

$$c/c_1 = \frac{\text{H} + \text{K}_1 + \text{K}_1\text{K}_2}{\text{H} + 2} (a) \quad \dots \quad (15).$$

(a) The development is essentially the same as given by Rosenstein for phenolphthalein (*Journ. Am. Chem. Soc.*, 1912, xxxvi., 1124).

Equations 11, 13, and 15 were tested by substituting the experimental values of the ratios c/c_1 and the hydrogen ion concentrations given for Solutions 1 and 4, Table V., in the equations, and solving for the constants K_1 and K_2 . The constants were then used to calculate the ratios for Solutions 2 and 3. In Table VI. are given the values of the ratios c/c_1 calculated from the various equations, and also the observed experimental ratios which are the averages of those given in Table V.

TABLE VI.
Values of c/c_1 .

Solution.	$\text{H}^+ \times 10^8$.	Observed.	Calc. by 11.	Calc. by 13.	Calc. by 15.
1.	2.533	2.23	2.23	2.23	2.23
2.	4.484	0.842	1.12	—	0.953
3.	10.53	0.293	0.371	—	0.308
4.	19.52	0.148	0.148	0.148	0.148

On the first assumption, namely, that the ion HIn^- is yellow and the ion $\text{In}^{=}$ is red, the ratios calculated by Equation 11, for Solutions 2 and 3, do not at all agree with the experimentally determined values. On the assumption that the intermediate ion HIn^- is red and the secondary ion $\text{In}^{=}$ is yellow, the constant K_2 , Equation 13, was found to be a negative quantity. This, in itself, proves the absurdity of the assumption; consequently, no ratios for Solutions 2 and 3 were calculated. On the assumption, however, that both the ions HIn^- and $\text{In}^{=}$ are red, the ratios calculated by Equation 15, agree fairly closely with the experimentally determined values. The agreement is as close as might be expected considering that in work of this character so many different sources of error are possible. The results lead to the conclusion, therefore, that rosolic acid acts as a dibasic acid, and furthermore, show that both the primary and secondary ions are intensely coloured.

In the case of phenolphthalein, it has been shown by Rosenstein (*loc. cit.*) that the coloured form of the indicator is only produced in appreciable quantity when the second hydrogen of the indicator acid is replaced by the base. This is in accord with the theory already referred to (*loc. cit.*), that the cause of the colour production is due to a combination between the metallic phenolate and the quinoid complex; since it is only where the second hydrogen is replaced that the formation of the quinoid phenolate complex is possible. In the case of rosolic acid, however, the quinoid phenolate complex can be found when the first hydrogen of the indicator acid is replaced by the base. The experimental fact, then, that the intensely coloured form of the indicator is produced when the first hydrogen is replaced by the base is perfectly in accord with the theories advanced.

Summary.

1. An intensification of the red colour of rosolic acid solutions incompletely transformed by the addition of alkali was found to take place when such solutions were allowed to stand, the time reaction being in all probability due to a slow union of the metallic phenolate with the quinoid complex.

2. In rosolic acid solutions containing a large excess of alkali a perceptible bleaching of the red colour was also indicated.

3. The ratio (c/c_1) of the red to the yellow component has been determined for indicator solutions of various hydrogen ion concentrations using the radiometric method developed in the original article (*loc. cit.*).

4. The values of the ionisation constant of rosolic acid calculated from the ratio c/c_1 , on the assumption that the indicator acid is monobasic, were found to decrease with decreasing alkalinity. When the hydrogen ion concentration was increased from 2.533×10^{-8} to 19.52×10^{-8} , the total salt concentration being 0.0259 N , the value of the ionisation constant K_1 was found to decrease from 5.65×10^{-8} to 2.89×10^{-8} .

5. It was found that this variation in the constants could be explained by regarding the indicator as a dibasic acid, and it was shown, furthermore, that the intensely coloured form of the indicator is formed when the first hydrogen of the indicator acid is replaced by the base.

RESEARCH AND PROGRESS IN AMERICAN MANUFACTURE.*

WHAT THE INVESTIGATOR HAS DONE AND CAN DO FOR INDUSTRIES.

By Dr. RAYMOND F. BACON, of the Mellon Institute of the University of Pittsburgh.

WHILE it is tacitly accepted by modern chemical industrialists that their manufacturing operations must be based upon research if they are to meet with success, is is not generally recognised that scientific research work conducted in the laboratory is the soul of industrial prosperity. However, much evidence of a convincing nature may be cited to show that research and progress are synonymous as applied to manufacturing.

The national Government, endowed institutions, and industrial establishments have advanced research on a business basis, but the public has not been taught to value it. This may be attributed to three causes:—(1) The work of the researcher, and especially the industrial researcher, is carried on in a quiet manner and is frequently of a secret nature; (2) the development of manufacturing is a very gradual evolution, each step of which is made possible by work which has been done before, and each step in advance of which is principally a natural evolution of what has preceded it; and (3) science has not received the proper treatment in magazines and newspapers, and consequently the readers thereof are not acquainted with the many ways in which science is co-operating with industry. That the calamity of the European conflict has served to direct the attention of the American public to the dependence of all of our industries of chemistry is purely incidental. The evolution of chemistry, and with it industrial research, has been proceeding rapidly during the past two decades, and has left its mark on the whole industrial development. American industries, whether chemical or metallurgical, are firmly established, rapidly growing realities, and the public should be acquainted with the principal factor involved in this growth.

Statisticians inform us that the progress of manufacturing in recent years is recorded in the patent literature. The technologist knows that this is incorrect, for such literature generally indicates those appliances and processes which cannot be kept secret. Nor can the progress of industry be traced by the imports, as stated for the chemical industry by Herstein (*Journ. Ind. Eng. Chem.*, 1912, iv., 328; *cf.*, Grosvenor, *Ibid.*, 1913, v., 686). A more definite relation exists between research and

* Address delivered at the National Exposition of Chemical Industries, Grand Central Palace, New York, September 25, 1915. From the *Scientific American Supplement*, No. 2081.

progress in manufacturing, although desirable statistics are wanting. Even though we cannot assert that the broadening of domestic production has been proportional to research, it may be said that the industrial profitability of to-day is derived from efficiency in production, and efficiency has resulted from research.

The Industrial Activity of the Chemist.

If it is conceded that chemistry is the intelligence department of industry (see Note), one may therefore conclude that the measure of the influence of the profession of the chemist upon the industrial development of our country constitutes *per se* an index of the value of research to manufacturing. I have pointed out in another place (*Science*, 1914, xl., 871), that the measure of a country's appreciation of the value of chemistry in its material development and the extent to which it utilises this science in its industries, generally measure quite accurately the industrial progress and prosperity of that country.

(NOTE.—This statement should not give rise to an impression that the contention is that the industrialist relies *absolutely* upon the chemist. The technical demands made by modern manufacturers are extensive and exacting, and sole reliance upon the chemist would be oftentimes fatal to the realisation of success. The aid of other industrial specialists must always be called in during the course of development).

As mentioned, the public has been left to its own resources to determine the function of that industrial scout, the chemist. This condition has been briefly explained by one chemist: "Our public work is obscured by impenetrable technical detail and our industrial achievements are cut off from public view by high factory walls." A large percentage of the 10,000 chemists of the United States do labour under cover, yet these 10,000 men—about 25 per cent of whom are engaged in industrial research, the others in control work—are actively occupied in manufactures which affect over 1,000,000 wage-earners and produce over 5,000,000,000 dol. worth of products. As Hesse (*Journ. Ind. Eng. Chem.*, 1915, vii., 294) has quite convincingly demonstrated, in the case of thirty-one American industries, the chemists employed therein directly affect 24.6 per cent of our manufacture values and 20.2 per cent of our values added by manufacture. They are constantly engaged in the development of processes and in refining methods of control or of manufacture.

The Evaluation of Industrial Research.

Many industrialists are even now certain that research will not pay. Some regard their technology as an hereditary art. Some have favourable raw material conditions or a large demand for their products, and are therefore disinclined to invest a very small portion of their earnings in a reserve of knowledge. Others have prospered because of high tariff, notwithstanding short-sighted management. But most of our industries are built upon stronger foundations. It is plain that the use of natural laws offers a more stable basis upon which to erect a manufacture and a more uniform source of profit than any structure built upon artificial conditions created by legislation. Moreover, the quality and value of a product are based upon the application of correct principles in its conception, preparation, and use, and the correct principles can only result from scientific research. Ample support to this contention is to be found in the manufacturing operations of to-day.

The Metallurgical Industries.

Turning first to metallurgy, one finds that the metals industrialists first called the service of research to their aid about 1885, to assist both in the perfecting of processes and the necessary mechanical equipment. In consequence whereof, zinc smelters eventually obtained the high extraction results, the low fuel consumption (by regenerative gas-firing), and the reduction of labour which characterise

their art to-day, and have made much progress toward the solution of their two great problems, the concentration of the ore and the treatment of flotation concentrate. Likewise, the scientist showed the copper industrialist how to make his metallurgical operations so constant that in the manufacture of refined copper the valuations of the product do not differ by more than 1 dol. in every 50,000 dol. worth of product; and research is now making promising progress in the development of flotation processes, in leaching of ores, in electrolytic deposition, and in electrolytic refining (especially in the treatment of anode slimes and in the recovery of by-products).

For twenty-five years the value of research chemists in improving mining operations and in concentrating, roasting, and smelting developments, has been appreciated, and each year a greater amount of money is expended by metallurgical companies for research than is in proportion to the increase in the production of ores. Those who desire to engage in mining are no longer deterred therefrom by the prospect of encountering a difficult metallurgical problem. The rapid progress in metallurgy during especially the last decade has inspired an abiding confidence and has aided more than all other factors combined in the extension of the mining industry. One prominent engineer has said (*Met. Chem. Eng.*, 1915, xiii., 522): "If I can only find the mine, I have little doubt of being able to develop a suitable treatment process." But even in the absence of the discovery of new mining districts, operators are seeking for neglected opportunities in the dumps and mines of abandoned districts, confident that the metallurgical difficulties of the past can be overcome by research.

(NOTE.—For a striking example of this metallurgical revival, see Parmelee's account of the cyanidation of low-grade sulphide ores in Colorado, *Met. Chem. Eng.*, 1915, xiii., 477).

The Manufacture of Iron and Steel.

To the valuable properties of the many alloys of iron now manufactured, from carbon steel to the complex alloy known as high-speed tool steel, which contains no less than five different elements apart from the iron itself, is to be attributed the great progress which has been made, whether in the arts of peace or in war. There is one simple concrete instance—the modern automobile. Eliminate the alloy steels used in its construction, and it could no longer be produced. The combination of lightness and strength necessary in such modern products is only made possible by the use of special alloy steels.

While the progress made in alloy steels since Hadfield's first researches in 1862 and onward has been wonderful indeed, the field for research is still an immense one, full of difficulties, disputed points, and important problems. It is true that there may not be at the present time room for such abnormal discoveries in ferrous metallurgy as in the past, but investigators are quietly and steadily augmenting our knowledge of iron and its alloys, and the value of such research work is generally recognised.

It remains to mention in this connection that the science of metallography, which has so materially aided the progress of metallurgy, has been developed by the assistance of that keen weapon of the physical chemist, the phase rule.

The Petroleum Industry.

Marked success has attended scientific progress in the refining of petroleum. Research has worked out processes for the dehydration and desulphurisation of crude oils and for the depolymerisation of heavy oils (especially the conversion of gas oils into motor fuel), and large refiners are now applying physico-chemical principles to the refining of oils, as instanced in tower stills (fractional condensation), the automatic control of temperatures during distillation and production of paraffin wax, and decolorisation of products by fuller's earth or bone-black. The employment of steam in the production of lubricating oils, the

process of continuous distillation, and the methods for chemically treating the products, are the results of research. More recent achievements in petroleum research are the production of drying oils from neutral oils and the synthetic preparation of fatty acids from crude oil. Then, too, it may be predicted that a simple, direct process for obtaining the butadiene hydrocarbons from petroleum will soon be found, and thus a good route to synthetic rubber will be opened up.

In the related asphalt industry, chemical research showed how asphaltoid bodies of much commercial importance might be prepared by the oxidation of petroleum, and the chemist has also given his aid in the preparation of suitable fluxes, in evolving a rational method of pavement construction, and in improving asphalt surfaces.

The Sulphuric Acid Industry.

The manufacturers of sulphuric acid and soda, the basis of all the other chemical industries, only attained to their full vigour after the various processes involved had been explained by research and after the most favourable conditions had been worked out. At the present time sulphuric acid is so extensively used that it is regarded as the gauge of the activity of the nation in chemical manufactures.

The first important practical improvement was made in the manufacture of sulphuric acid in this country so early as 1814, when platinum stills were introduced for the concentration of the acid. Later the process was made continuous, and many improvements rapidly followed. Then the contact process, the development of the great industrial researcher, Winkler, was introduced and improved. And finally we have the industrially important process for obtaining sulphuric acid from smelter gases. In 1913, about 22 per cent of the total sulphuric acid produced in the United States was recovered from the gases from copper and zinc smelters.

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, December 2, 1915.

Sir J. J. THOMSON, O.M., President, in the Chair.

PAPERS were read as follows:—

"Existence of Converging Sequences in certain Oscillating Successions of Functions." By W. H. YOUNG, F.R.S.

"Emulsifying Action of Soap: A Contribution to the Theory of Detergent Action." By S. A. SHORTER and S. ELLINGWORTH.

1. The hydrolysis alkali in a soap solution is capable of assisting in the formation of the soap absorption layer by interacting with free fatty acid in an oil.

2. The "surface activity" of the hydrolysis alkali, in case of oils containing small amounts of free fatty acid, is much smaller than that of the undecomposed soap.

3. Surface activity of free alkali in soap solution is less than that of the same concentration of alkali in water.

4. Addition of alkali to soap solution increases surface activity of soap. This effect is much too large to be explained by suppression of hydrolysis. It is suggested that the effect is due to increase in colloidal nature of "semicolloidal" soap solution.

"The Newtonian Constant of Gravitation as affected by Temperature." By P. E. SHAW.

1. It has been found possible (a) to obtain consistent cyclic readings in a gravitational experiment of the

Cavendish type, even though the large masses are maintained for hours above 200° C., while the small masses remain at ordinary temperatures; (b) to carry on this investigation in the centre of a city at any time by day or night, in spite of tremors and the special disadvantage of having the torsion balance in a vacuum.

2. The conclusion reached is that there is a temperature effect of gravitation. When one large mass attracts a small one the gravitative force between them increases about 1/500 as temperature rises from, say, 15° to 215°. Provisionally the result is stated as $+1.2 \pm 10^{-5}$ per 1° C. The readings are not steady enough to justify the statement that there is a linear relation for G/θ . Time may be a factor in the effect, but the net result has not been shaken by a long series of tests.

3. The above result, though new, is not entirely unsupported by other experiments, for previous work yields indirect evidence of a positive temperature coefficient. The weight experiments of Poynting and Phillips, which yielded negative results, are not strictly comparable with the author's.

4. As a by-product of these experiments it was found that silver bars of the highest purity, after being heated to 130° C. and kept in a strong magnetic field, were permanently though weakly magnetised, and that the coercivity was considerable.

"Skin Friction of the Wind on the Earth's Surface."
By G. I. TAYLOR.

The amount of the skin friction between the wind and the surface of the earth is calculated from observations of wind velocity at different heights above the ground. It is found that the skin friction force acting on unit area of the ground is proportional to the square of the wind velocity, and that its actual value is of the same order as, though probably smaller than, that found by experimenting with flat plates and pipes in the laboratory.

The object with which the investigation was undertaken was to find out whether the skin friction on a small surface is nearly equal to that on a very large surface, but if it were assumed that this is the case, the method employed furnishes an explanation of the fact that the surface wind is on the average roughly about half the gradient wind in the latitude of the British Isles.

CHEMICAL SOCIETY.

Ordinary Meeting, November 4, 1915.

Dr. ALEXANDER SCOTT, M.A., F.R.S., President, in the Chair.

THE PRESIDENT referred to the loss sustained by the Society, through death, of Messrs. Charles Maurice Berlein (killed in action), Henry Crookes, John Gill, Tamemasa Haga, Christopher Hodgson, Frank Jagger, Vivian Byam Lewes, John George Lyon, Sir Andrew Noble, Bart., Hugo Schiff (Honorary and Foreign Member).

In a statement made as to the work carried out by the Society during the Vacation, the PRESIDENT mentioned that 1147 Fellows had returned the forms issued in the letter sent out on July 1; these forms had now been classified, and the offers of assistance tabulated. Many Fellows had offered to engage in the manufacture of munitions, but at present only those who can devote the whole of their time to the work are wanted. There is considerable difficulty in making use of the spare time offered by Fellows, but a careful record has been kept of all such offers, which will be used whenever possible.

A large number of suggestions had been received and had been considered by the Council. All such suggestions as were deemed of value were submitted either to the Special Committees appointed by the Council or to the proper Government Departments. In many cases the Authorities had expressed their appreciation of the services rendered by the Society in this direction.

Reference was made to the letter issued on October 29, calling attention to a Scheme for the Organisation and Development of Scientific and Industrial Research published by the Government as a White Paper. Fellows are invited to forward to the Council suggestions for suitable researches.

Mr. F. G. Henderson was formally admitted a Fellow of the Chemical Society.

Certificates were read for the first time in favour of Messrs. Basil Albert Adams, 118, High Street, Beckenham; Alfred Anderson, Hamer House, Egerton, Bolton; William Archibald Andrews, B.Sc., 22, The Avenue, Carmarthen; Frederic Sutcliffe Aumonier, B.Sc., Rousden Cottage, Bushey Heath, Watford; Thomas Hedley Barry, 9, Napier Avenue, Fulham, S.W.; William Arthur Bush, 100, William Street, New York City, U.S.A.; Joseph Herbert Canning, Crindan Gasworks, Newport, Mon.; Owen Colverd, 52, Crofton Road, Plaistow, E.; Sydney Francis William Crundall, 28, Marlborough Hill, Harrow; Bhaskar Balvant Dhavale, M.A., Kolhapur City, Bombay Presidency, India; Pavitra Kumar Dutt, M.A., M.Sc., 53, Lofthouse Place, Leeds; Sudhamoy Ghosh, D.Sc., 45, Rupnarayan Nandau Lane, Bhowanipur, Calcutta, India; Charles Stanley Graham, 174, Frodingham Road, Scunthorpe, Lincs.; James Kendall, D.Sc., Chemistry Department, Columbia University, New York City, U.S.A.; William Kitto, 366, City Road, E.C.; Thomas McLachlan, 23, Clarendon Road, Lewisham, S.E.; John Livingston Michie, 1, Duke Street, Hawick; Elton Arthur Nash, care of Messrs. J. Godden and Co., Curaçao, Dutch W. Indies; Archibald Durrant Ollé, 28, Charlotte Street, Ashfield, N.S.W.; James Walker Porter, 35, Templemore Avenue, Belfast; Alfred Potter, 16, Nelson Street, Lower Broughton, Manchester; George Scott Robertson, M.Sc., East Anglian Institute of Agriculture, Chelmsford; Fred Robinson, B.Sc., 32, Hovingham Grove, Harehills, Leeds; Godfrey Edward Scharff, B.A., Research Laboratory, Petaling, Federated Malay States; Hugh Wolseley Thomas, 9, Dalhousie Square, Calcutta, India; Henry Burroughs Tilden, Poste Restante, Bombay, India; Mohammad Sana Ullah, B.A., M.Sc., 82, Highbury New Park, N.; George Walworth, B.A., Harper Adams, Agricultural College, Newport, Salop; Willis John Williams, Essendon, Turner Avenue, Haberfield, via Sydney, N.S.W.

The following papers were read:—

"Reactions between the Higher Fatty Acids and Salts of the Lower Fatty Acids." By ARTHUR WILLIAM KNAPP and RAYMOND VARIAN WADSWORTH.

"The Interaction of Perchloric Acid and Potassium Sulphate as an example of Reversible Change." By WILLIAM ALFRED DAVIS.

"The Study of the Density and Viscosity of Aqueous Solutions with Special Reference to Nitric Acid. Part II. Viscosities." By WILLIAM ROBERT BOUSFIELD.

"The Formation and Preparation of Glucosemonoacetone." By JAMES COLQUHOUN IRVINE and JAMES LESLIE AULD MACDONALD.

Ordinary Meeting, November 18, 1915.

Dr. ALEXANDER SCOTT, M.A., F.R.S., President, in the Chair.

THE PRESIDENT referred to the loss sustained by the Society, through death, of James Louis Foucar (killed in action) and Raphael Meldola.

The PRESIDENT referred to the important rôle Prof. Meldola had played in furthering chemical science and to his valuable services to the Society.

Prof. Meldola served continuously on the Council for over a quarter of a century; he was Foreign Secretary from 1891 to 1902, and held the office of President from 1905 to 1907.

The following announcements were made:—

1. That the Council had decided to hold the Ordinary Scientific Meetings at 8 o'clock instead of at 8.30 p.m., as from December 2.

2. That the Société Helvétique des Sciences Naturelles held its 100th Anniversary at Geneva from September 12 to 15, 1915, but owing to the war the usual invitation had not been issued to Foreign Scientific Societies or to Chemists residing out of Switzerland.

3. That a photograph of the late Dr. Hugo Schiff had been received from Mrs. Schiff, and that Prof. Edward Kinch had presented photos of Sir Joseph Gilbert and Sir John Bennet Lawes.

Mr. F. R. Ennos was formally admitted a Fellow of the Chemical Society.

Certificates were read for the first time in favour of Messrs. Harry Dean, Oak Villa, Greenhead Road, Huddersfield; Robert Ensoll, 148, Devonshire Avenue, Southsea, B.O., Portsmouth; Fred Fairbrother, B.Sc., 8, Benfield Street, Heywood; Philip Lelean, F.R.C.S., D.P.H., Royal Army Medical College, Millbank, S.W.; Leroy Wiley McCay, The Library, Princeton University, Princeton, N.J., U.S.A.; Donald John Matthews, care of The Marine Biological Association, Citadel Hill, Plymouth.

The following Certificates have been authorised by the Council for presentation to ballot under By-law I. (3):—Warwick Oben Gurney Trehair, 34, 2nd Avenue, Durban, Natal, S. Africa; Harry Maas Ullmann, Ph.D., Lehigh University, S. Bethlehem, Pa., U.S.A.; Kadayam Chudamani Viraraghavan, M.A., Hindu College, Tinnevely, Madras, India.

Dr. E. J. RUSSELL delivered a lecture entitled "*The Principles of Crop Production*." A discussion took place at the conclusion of the lecture, and the PRESIDENT then proposed a vote of thanks to Dr. Russell, which was carried with acclamation.

PHYSICAL SOCIETY.

Ordinary Meeting, November 26, 1915.

Dr. A. RUSSELL, M.A., Vice-President, in the Chair.

A PAPER on "*Obtaining and Maintaining a Bright Hydrogen Spectrum, with Special Reference to the 4341 Line*" was read by Mr. J. GUILD, F.R.A.S.

The paper treats of the conditions of pressure, discharge, &c., most suitable for the production of a bright hydrogen spectrum, such as is required for refractometry and similar purposes. The rapid deterioration of the tubes with use is shown to be caused by a rise of pressure due to the evolution of hydrogen by the electrodes. The trouble may be obviated by sealing an auxiliary bulb of 1½ or 2 litres' capacity to the discharge tube. This reduces the rate of pressure variation and prolongs the useful life of the tube nearly a hundredfold. The use of capacity and inductance is shown to be very helpful with partially deteriorated tubes.

DISCUSSION.

Mr. F. E. SMITH asked if the hydrogen could not be expelled from the electrodes before sealing off.

Mr. S. D. CHALMERS said he had had a similar experience with the deterioration of hydrogen tubes. He was surprised that the author found all the lines to be most satisfactory at the same pressure. He had sometimes found it convenient to use different tubes for the C and G' lines.

Mr. G. H. GARDINER mentioned that when taking some photographs of vacuum tube spectra he had been struck with the rapid deterioration of some of the ultra-violet lines. This had been traced to the formation of a scarcely perceptible deposit on the quartz window due to the scattering of the electrodes, and he thought a similar cause might be sufficient to account for the decay of the violet hydrogen line.

Prof. J. W. NICHOLSON thought the paper, although written from another point of view, formed a useful contribution to the knowledge of the conditions under which different spectra of the same gas were produced. The hydrogen spectrum was a difficult one to deal with, and anything which threw additional light on it was welcome.

Mr. D. OWEN referred to the rapid rise in the heating of the glass near the electrodes at pressures under 1 mm. What happened at still lower pressures? Presumably the rise could not go on indefinitely, as under the conditions of the experiment the current decreased as the exhaustion progressed.

The AUTHOR, in reply, said he had tried to get rid of the hydrogen occluded in the electrodes before detaching the tube from the pump, but without success. His experience, that all the lines attained their maximum brightness at the same pressure, was borne out by all other observers who had made quantitative observations. A tube which does not show any G' may still have plenty of C and F on account both of the greater energy of these lines and of their greater visibility, but he could not conceive of a tube having a usable G' being deficient in either C or F. It was shown conclusively in the paper that the deterioration was due to pressure changes. No "imperceptible" deposit could affect lines in the visible spectrum, however effective it might be in the case of those in the ultra-violet. Moreover, no deterioration due to deposits on the glass or to the condition of the capillary would be retarded in the least by the addition of an auxiliary volume.

A paper on "*The Determination of the Coefficient of Diffusion of Potassium Chloride by an Analytical Method*," by A. GRIFFITHS, J. M. DICKSON, and C. H. GRIFFITHS, was read by Dr. GRIFFITHS.

This paper represents an attempt to develop an analytical method of determining the coefficient of diffusion of a salt in water capable of giving consistent and accurate results.

The lower ends of a number of vertical and parallel diffusion tubes end in a reservoir of large capacity containing a solution of potassium chloride. The greater part of the reservoir is above the lower ends of the tubes, and by gravity the solution at the lower ends is kept at an approximately constant concentration. The upper ends of the tubes are covered with a cap, provided with an outlet and an inlet tube. Water enters the tap by the inlet tube, and a weak solution, containing the diffused salt, leaves the cap by the outlet tube. Time, which may be as long as a fortnight, is allowed for the attainment of the steady state, and an individual experiment may last six weeks. The quantity diffused is obtained by chemical analysis. In the case of a solution containing 0.2237 grm. of potassium chloride to the cubic centimetre (a 3N solution) the "mean diffusivity" with respect to water is 1.703×10^{-5} (C.G.S. units) at a temperature of 18.5°C .

DISCUSSION.

Mr. B. W. CLACK said that the difference of 10 per cent between the authors' results and those obtained by him was not nearly so great as the discrepancies between the results of other workers on similar solutions. He showed slides containing the tabulated results of other observers for solutions of KCl and NaCl. These differed from one another by 20 to 30 per cent. He believed Dr. Griffiths had had some difficulty at first in the analysis of the dilute solutions. The method by which he had overcome this was, he thought, noteworthy.

Dr. S. W. J. SMITH said he was interested in diffusion from the point of view of electrolytic phenomena. The way in which the diffusion depends on the concentration for different salts had an important bearing on the electrolytic behaviour of dilute solutions.

Dr. T. BARRATT asked if variations of temperature might not account for the discrepancy between the authors' results and those of Mr. Clack. The temperature coefficient appeared to be about 7 per cent for 3°C . Was it certain that in both methods the temperature was main-

tained constant to within this amount for the periods of six weeks or so required for an experiment? There was another effect of temperature variations. Any expansion of the solution in the reservoir had to take place through the diffusion tubes, and this would affect the results very seriously.

Dr. GRIFFITHS, replying for the authors, said that the temperature had been kept constant to within 0.5°C . He had gone into all the possible errors due to temperature variations, and they were not comparable with the 10 per cent question. His convective method gave results about 4 per cent lower than the analytical method.

An Apparatus for Evaluating Elliptic Integrals was exhibited by Mr. A. F. RAVENSHEAR.

The apparatus produces by mechanical means a graph of the integral in rectangular co-ordinates. The graph is made by a hatchet scriber, which is controlled as regards direction, but is otherwise free to move anywhere over the surface of the paper. Taking the third integral as an example—

$$y = \int \frac{1}{(1 + a \sin^2 \theta) \sqrt{1 - c^2 \sin^2 \theta}} d\theta.$$

The apparatus comprises (1) the scribing appliance; (2) a mechanism which evaluates $\sqrt{1 - c^2 \sin^2 \theta}$, where θ is the value of the abscissa of the middle point of the hatchet; (3) a mechanism which determines a length equal to the product $(1 + a \sin^2 \theta) \sqrt{1 - c^2 \sin^2 \theta}$; and (5), a director which is variably inclined to the axis of X, so that the tangent of its inclination is negative and equal to the above-mentioned product. By a parallel linkage, a line in the hatchet plate at right angles to the hatchet is kept parallel to the director, so that the hatchet has an inclination Φ to the axis of X such that—

$$\tan \Phi = \frac{1}{(1 + a \sin^2 \theta) \sqrt{1 - c^2 \sin^2 \theta}}$$

Since the hatchet is always tangent to the graph which it describes, $dy/dx = \tan \Phi$, whence—

$$y = \int \frac{1}{(1 + a \sin^2 \theta) \sqrt{1 - c^2 \sin^2 \theta}} d\theta.$$

By suitable adjustments the apparatus deals in a similar way with the first and second integrals.

DISCUSSION.

Dr. A. RUSSELL thought the instrument was very ingenious and likely to be of the greatest utility. The third elliptic integral was of frequent occurrence in electrical engineering and in hydrodynamics, and an apparatus for its easy evaluation would be welcomed by many.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, December 1, 1915.

Mr. A. CHASTON CHAPMAN, President, in the Chair.

Dr. Eric Keightley Rideal and Mr. Arthur Sidney Carlos were elected Members of the Society.

Certificates were read for the first time in favour of Messrs. Thomas John Hichcock and Nelson Trafalgar Foley.

Certificates were read for the second time in favour of Messrs. Thomas Featherstone Harvey, Cyril Herbert Manley, Caryl Cameron Roberts, and Frank Thomas Shutt.

The following papers were read:—

"The 'Presumptive Coli Test' on Unchilled Waters." By W. PARTRIDGE, F.I.C.

The author points out that if positive results are ignored and negative results only considered, the "Presumptive

B. coli Test" often usefully supplements the ordinary chemical analysis of unchilled water.

"Notes on Methods of Analysing Oleaginous Seeds and Fruits." By E. RICHARDS BOLTON.

It is shown that the errors in the estimation of oil in oleaginous seeds and fruits (copra in particular) are due rather to "sampling" than to actual analysis. Methods of sampling, grinding, and analysis were demonstrated to show that, while the oil in copra could be estimated with great accuracy by the methods given, a departure from the procedure would be liable to cause considerable error.

SOCIETY OF CHEMICAL INDUSTRY (LONDON SECTION).

Ordinary Meeting, December 6, 1915.

Mr. ARTHUR R. LING in the Chair.

The CHAIRMAN, in opening the meeting, referred to the loss the Society had sustained by the death of Prof. Raphael Meldola and Prof. Vivian B. Lewes. Prof. Meldola, he said, was one of the Society's most illustrious past Presidents, and the loss of him to the country at the present time was a very serious one.

A paper was read by Prof. DONNAN, entitled "Geometry of Blending."

The author discussed the graphical solution of the following problem:—Suppose a product, which is a mixture, is manufactured from raw materials, X.Y.Z., &c., of fluctuating price, and that a product of determinate quality can be manufactured from different proportions of the raw materials. What are, for any given prices, the correct proportions to employ so that the cost of the raw materials per unit weight of product of determinate quality shall be as low as possible? The author gave the general geometrical solution of this problem for the case of $n=3$, and showed by diagrams how the graphical solution could be carried out practically. It was pointed out that the problem of blending in one form or another occurred in many industries, e.g., the manufacture of soap, glass, pottery, varnish, adhesives, lubricants, &c.

The intention of the author is to direct the attention of technical chemists to the value of geometrical methods in the solution of many classes of technical problems, and the particular problem selected in the paper is only one example out of hundreds of similar ones.

Mr. T. C. CLOUD read a paper entitled "The Transport of Material in the Form of Dust." The application of the principle of the vacuum cleaner was advocated for the removal in a factory of different kinds of dust. The author dealt more particularly with the removal of arsenical dust.

A paper on "Sampling and Analysis of Beeswax," in the absence of the author, was taken as read.

NOTICES OF BOOKS.

Elementary Practical Metallurgy. By J. H. STANSEIE, B.Sc. (Lond.), F.I.C. London: J. and A. Churchill. 1915.

THIS book provides a short course in practical metallurgy which can easily be adapted to the needs of different classes of students. Practically no knowledge of chemistry is presupposed, but in the introductory section the very simplest apparatus and operations are described and illustrated. The analysis of fuel and the determination of calorific power are treated in the next chapter, which is followed by a description of the examination of refractory materials and of the formation and reduction of oxides and sulphides. Methods of mechanical testing are then concisely discussed, and with this chapter the general part of the book

concludes. The non-ferrous alloys and metals, iron and steel, and gold and silver are the subjects of the last three chapters, which are quite independent of one another, so that the student who intends to specialise in any branch can confine his attention to that alone.

The British Coal-tar Industry; its Origin, Development, and Decline. Edited by WALTER M. GARDNER, M.Sc., F.I.C. London: Williams and Norgate. 1915.

THE topics with which this book deals are of such vast importance to the welfare of the nation that anybody who aids its circulation will be a real benefactor to his country. Unfortunately it seems not improbable that only those who are in hearty agreement with almost every statement it contains will read it, for even now the general public, the politician, and the manufacturer usually regard any scientific subject with a feeling largely composed of mingled contempt and distrust. The book contains reproductions either in full, or in some cases slightly abridged, of all the lectures and addresses on the coal-tar industry given in this country since Perkin established it in 1856. The first twenty-two lectures are mainly historical, and are arranged chronologically, beginning with the Cantor Lectures delivered by Sir William Perkin in 1868. The artificial production of indigo is a subject which was discussed at the Royal Institution by Sir Henry Roscoe in 1881, and a short résumé of the indigo crisis has also been prepared from various lectures and writings. The last ten papers deal with the problem as viewed in the light of the present day, and the value and importance of this collection of the views of experts cannot be over-estimated. One of the most striking of the addresses which have been reprinted is that given at Manchester in 1914 by Lord Justice Moulton, on the manufacture of dyes in England, but it is perhaps invidious to select any for special mention when so much sound advice, such clear well-balanced warnings and suggestions abound in every lecture.

The Rugby Course of Elementary Chemistry. By H. P. HIGHTON, M.A. London: Edward Arnold. 1915.

THIS course of elementary chemistry is intended to cover two school years' work, beginning at the beginning. The plan of the book is thoroughly practical, and the author appears to have skillfully incorporated in it the best features of the didactic and heuristic methods. The course is divided into 66 lessons; in each case a short lecture syllabus is given, describing very briefly the experiments to be performed before the class, and indicating to the teacher what descriptions and explanations he should give. These notes are followed by illustrated accounts of the practical work to be done in the laboratory by each boy. The directions are always full enough to require practically no supplementing by the teacher and the apparatus involved is cheap and simple and easily fitted up by the boy himself. Some of the practical devices are decidedly neat and ingenious. The subjects studied include oxygen, hydrogen, carbon, nitrogen, sulphur, and the halogen elements, with a little theoretical work. Thus the scope is perhaps rather narrow, considering that the work is to be extended over two years, but, on the other hand, a really sound foundation would be laid and the pupil would receive a thorough training in manipulation and simple experimental work.

Messrs. Abdulla and Co., Ltd., the well-known cigarette specialists, have issued a novel almanac for 1916, containing twelve coloured reproductions of drawings and paintings by well-known artists, some from this year's Royal Academy. The subjects selected are those connected with current events, and Messrs. Abdulla and Co. are to be congratulated upon the originality of the idea. We understand that 20,000 copies have been placed at the disposal of the British Red Cross Society for sale, the proceeds to go to their funds.

CORRESPONDENCE.

PREPARATION OF SULPHURETTED HYDROGEN.

To the Editor of the Chemical News.

SIR.—The device described by Mr. Ellis in the CHEMICAL NEWS of November 19 (cxii., 258) was adopted in our laboratories a good many years ago, and will be found in the CHEMICAL NEWS for May 3, 1907 (xcv., 207). My apparatus has since then been improved and simplified by substituting fused-in glass connections and a ground-glass stopper for the rubber corks of the original design, and is now on the market.—I am, &c.,

F. SOUTHERDEN.

Royal Albert Memorial,
University College, Exeter, Dec. 6, 1915.

INTRODUCTION TO THE THEORY OF
RELATIVITY.

To the Editor of the Chemical News.

SIR,—Referring to the above article, there are a few typographical slips that escaped my notice. On p. 236, col. 2, line 21 from bottom, "Minskowski" should read Minkowski. On p. 249, col. 1, insert 1 in the gap before the minus sign. The formula in the footnote on p. 261, " n_2 " should read n^2 ; and in col. 2 of the same page, line 30 from bottom, "p. 154" should read p. 594.—I am, &c.,

F. H. LORING.

CHEMICAL NOTICES FROM FOREIGN
SOURCES.

Bulletin de la Société Chimique de France.
Vol. xvii.-xviii., No. 12, 1915.

New Cupric Compound of Glycocoll.—J. Ville.—When glycocoll is treated with a solution of copper sulphate and potash a dark blue liquid is obtained, which on addition of alcohol gives a precipitate of fine blue needles of copper glyccolate, $(\text{NH}_2\text{CH}_2\text{CO}_2)_2\text{Cu} \cdot \text{H}_2\text{O}$. In absence of potash the results vary according to the proportions of glycocoll and copper sulphate. If the former is present in excess the blue needles of glyccolate are obtained, accompanied by colourless prisms of glyccoll sulphate. If the proportions are two molecules of glyccoll to one of copper sulphate the addition of alcohol makes the liquid turbid, and drops of a thick heavy dark blue liquid separate. This blue liquid is very soluble in water, insoluble in alcohol, ether, benzene, and chloroform. In a dry vacuum it gives a resinous hygroscopic dark blue residue, which on analysis gives results which indicate that it contains two molecules of glyccoll and one of anhydrous copper sulphate. It is a sulphuric compound of cupric glyccolate, $\text{SO}_4\text{H}_2(\text{NH}_2\text{CH}_2\text{CO}_2)_2\text{Cu}$, and can also be obtained by the direct union of sulphuric acid and copper glyccolate.

No. 13—14, 1915.

Thermal Analysis of Binary Mixtures.—Emile Baud.—The author has already shown that the thermic effect due to the mixture of x molecules of a liquid A with $1-x$ molecules of B (there being no chemical action between the two liquids), is given by $\Delta q = kx(1-x)$ analogous to the equation given by Biron for the change of volume Δv which accompanies the mixture of two liquids. For variations of volume the equation is often incorrect, but for the same mixtures it gives satisfactory results for the quantities of heat. When some mixtures are made heat is disengaged, and sometimes heat is absorbed or disengaged according to the proportions of the constituents. It seems probable that purely physical mixtures occur with absorption of heat, according to the

equation $\Delta q = kx(1-x)$, and that in the cases in which this equation is not followed chemical phenomena, depolymerisations, or combinations occur.

MISCELLANEOUS.

Royal Institution.—The following are the Lecture Arrangements at the Royal Institution before Easter:—Prof. H. H. Turner, a course of six illustrated lectures, adapted to a juvenile auditory, on "Wireless Messages from the Stars": How the Messages are Carried, December 28; How the Messages are Received, December 30; First Message, January 1; Second Message, January 4; Third Message, January 6; Fourth Message, January 8. Prof. Charles S. Sherrington, six lectures on the Physiology of Anger and Fear, and Nerve Tone and Posture. Prof. Edward J. Russell, two lectures on the Plant and the Soil; Prof. Arthur Keith, two lectures on Sea Power as a Factor in the Evolution of Modern Races; Prof. Frederick Keeble, three lectures on Modern Horticulture; Prof. W. A. Bone, three lectures on Utilisation of Energy from Coal; Sir F. Watson Dyson, Astronomer Royal, on Measurement of the Brightness of Stars; Prof. L. W. King, two lectures on Recent Excavations in Mesopotamia; Prof. Henry E. Armstrong, two lectures on Organic Chemistry in War; Dr. W. H. Hadow, three lectures on English Music in the Tudor Period; Charles J. Holmes, two lectures on Raphael and Michael Angelo; Sir Sidney Lee, two lectures on the Shakespeare Tercentenary; Hon. John Fortescue, three lectures on Eminent Generals of the Last Great War; Prof. Sir J. J. Thomson, six lectures on Radiation from Atoms and Electrons. The Friday Evening Meetings will commence on January 21, when Prof. Sir James Dewar will deliver a discourse on Problems in Capillarity. Succeeding discourses will be given by Leonard Hill, Prof. William Bateson, Prof. Gilbert Murray, Prof. Ernest G. Coker, Prof. Sir Arthur Quiller-Couch, Prof. Silvanus P. Thompson, Sir Napier Shaw, Dr. Aubrey Strahan, Prof. W. M. Bayliss, Prof. A. Fowler, Wilfrid Ward, and Prof. Sir J. J. Thomson.

Metals and Munitions.—Brass, copper, zinc, aluminium, nickel, and other non-ferrous metals being of such enormous importance in the production of munitions, it is not surprising to learn that the Institute of Metals (which takes within its purview these and all other metals except iron and steel) is very closely concerned with the production of the thousand and one metal articles required for the successful prosecution of the war. The Institute is in daily touch with many of the munition factories throughout the country, and also with certain Government Departments requiring metallurgical information. As an indication of the utility of the publications of the Institute of Metals (particularly at the present time) it may be mentioned that large shipments of the *Journal of the Institute of Metals*, in which are recorded the very latest scientific methods of dealing with the non-ferrous metals, are being despatched to Japan and the United States for use in works engaged in producing munitions for the Allies. In addition, volumes are being sent to various public and university libraries located in the United States' munitions centres. German submarines have taken toll of large consignments which were sunk in the *Hesperian* and the *Arabic*, but duplicate sets of volumes have now replaced those lost in this manner. The volumes are supplied gratuitously to members—numbered among whom are most of our important munitions makers—but copies can be purchased by non-members from the offices of the Institute of Metals, Caxton House, Westminster.

MEETINGS FOR THE WEEK.

TUESDAY, 21st.—Institution of Petroleum Technologists, 8. "The Uralsk Province and its Oilfields," by F. A. Holiday.

THE CHEMICAL NEWS.

Vol. CXII., No. 2926.

THE CONDUCTIVITY AND VISCOSITY OF SOLUTIONS OF ELECTROLYTES IN FORMAMID.*

By P. B. DAVIS, W. S. PUTNAM, and HARRY C. JONES.

(Continued from p. 298).

Discussion of Results.

TABLES III. to XXII., inclusive, give the molecular conductivity, dissociation, viscosity, and fluidity, as well as the temperature coefficients both of conductivity and fluidity for all the salts studied.

In this laboratory, during the past fifteen years, solutions in the following pure solvents have been investigated:—Water, methyl and ethyl alcohols, acetone, and glycerol. Among the results of this work in pure solvents are the discovery or confirmation of many relations between the conductivity and viscosity of solutions, the dissociation of the solutes, and the dielectric constant, association factors, and viscosities of the solvents. (These results have been tabulated and discussed in *Publications* Nos. 170, 180, and 210 of the Carnegie Institute). Reference to Table II. shows that formamid is a solvent markedly different from any other pure solvent investigated, in regard to the three constants mentioned. The most important result of this investigation is that the evidence it has developed supports and confirms all the relations and conclusions that have been worked out by Jones and his co-workers, from their investigations with other pure solvents. These relations will be discussed in turn.

The Thomson-Nernst theory (*Phil. Mag.*, 1893, xxxvi., 320; *Zeit. Phys. Chem.*, 1894, xiii., 531) is that the forces which hold the atoms together are electrical; hence the solvent having the highest dielectric constant has the greatest dissociating power. The dissociating power of solvents is shown in two ways:—First, by comparing the percentage dissociation of solutions having the same normality, and, second, by comparing the dilutions at which complete dissociation is reached. Compare Table VII. with the following:—

Aqueous Potassium Iodide Solution at 25.

V.	Temperature percentage coefficient 25° to 35°.		
2	112.8	76.6	1.85
8	120.7	82.0	1.97
2048	147.2	100.0	2.04

Table VII. shows that the dissociation of the N/2 solution of potassium iodide in formamid is only 71 per cent at 25°. From the data we calculate that the viscosity of the N/2 solution is 12.4 per cent greater than the solvent, while the viscosity of N/2 solution of potassium iodide in water is known to be less than that of the solvent. From a large mass of evidence we know that viscosity is by far the largest factor affecting conductivity in solutions in which dissociation is of the same order of magnitude. The conductivity of the N/2 solution in formamid at 25° is 18.67. We can assume without appreciable error that if the viscosity of the solvent and the N/2 solution were in the same ratio as in the case of the potassium iodide solution in water, the conductivity of the N/2 solution in formamid would be at least 12.4 per cent larger than the figure given—18.67. Recalculating the dissociation of the potassium iodide-formamid solution on this basis gives 79.4 per cent, compared with 76.6 per cent for the potassium iodide solu-

tion in water. This latter figure would be even less if corrections were made for the fact that the viscosity of an N/2 solution in water is less than that of the solvent, which would be a legitimate correction to make for the purpose of this comparison. Comparing in this way the dissociation of these two N/2 solutions, we find, as would be expected from the Thomson-Nernst theory, that formamid has the greater dissociating power.

Complete dissociation of potassium iodide in formamid is found in the N/200 solution, while in water it is not reached till the N/2048 solution. Therefore, in both respects, formamid falls in line with the Thomson-Nernst theory. This relation is confirmed by every salt studied in this investigation for which data for comparison are available. The rubidium salts show the stronger dissociating power of formamid much more than some others that were studied.

TABLE IX.—Ammonium Bromide in Formamid.

V.	Molecular conductivity.			Dissociation.		
	15°	25°	35°	15°	25°	35°
2	16.31	20.85	25.79	70.6	70.6	70.0
4	18.21	23.31	28.88	78.8	78.9	78.3
10	20.57	26.21	32.53	89.0	88.7	88.3
50	21.82	27.94	34.82	94.4	94.6	94.5
200	22.63	28.83	35.93	97.9	97.6	97.5
400	23.11	29.54	36.86	100.0	100.0	100.0
K	2.94 × 10 ⁻⁵	3.76 × 10 ⁻⁵	4.67 × 10 ⁻⁵			

Viscosity and Fluidity.

V.	η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°
2	0.04795	0.03607	0.02776	20.86	27.73	36.02
4	0.04550	0.03455	0.02680	21.98	28.94	37.31
10	0.04399	0.03273	0.02635	22.73	30.55	37.95
Solv.	0.04304	0.03256	0.02542	23.23	30.71	39.34

TABLE X.—Ammonium Iodide in Formamid.

V.	Molecular conductivity.			Dissociation.		
	15°	25°	35°	15°	25°	35°
2	16.90	21.70	26.80	73.6	73.1	72.5
4	18.78	24.06	29.88	81.8	81.0	80.8
10	20.48	26.32	32.44	89.2	88.6	87.7
50	21.31	27.39	33.92	92.8	92.3	91.2
100	22.20	28.40	35.40	96.7	95.7	95.8
400	22.96	29.69	36.97	100.0	100.0	100.0
K	3.68 × 10 ⁻⁵	4.71 × 10 ⁻⁵	5.87 × 10 ⁻⁵			

Viscosity and Fluidity.

V.	η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°
2	0.05091	0.03856	0.03007	19.64	25.93	33.26
4	0.04571	0.03417	0.02669	21.88	29.27	37.47
10	0.04367	0.03311	0.02607	22.90	30.20	38.36
Solv.	0.04201	0.03207	0.02496	23.80	31.18	40.06

TABLE XI.—Tetramethyl Ammonium Chloride in Formamid.

V.	Molecular conductivity.			Dissociation.		
	15°	25°	35°	15°	25°	35°
2	14.62	18.72	23.38	68.6	68.5	68.1
4	16.92	21.80	27.27	79.4	79.7	79.4
10	18.37	23.65	29.32	86.2	86.5	85.4
50	19.64	25.32	31.65	92.1	92.6	92.1
200	21.19	27.34	34.11	99.5	100.0	99.3
400	21.30	27.34	34.35	100.0	100.0	100.0
K	1.53 × 10 ⁻⁵	1.99 × 10 ⁻⁵	2.46 × 10 ⁻⁵			

Viscosity and Fluidity.

V.	η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°
2	0.04775	0.03578	0.02791	20.94	27.95	35.83
4	0.04503	0.03427	0.02679	22.21	29.18	37.33
10	0.04394	0.03313	0.02601	22.76	30.18	38.45
Solv.	0.04274	0.03194	0.02511	23.40	31.31	39.83

* From the *Journal of the Franklin Institute*, November, 1915.

TABLE XII.—Tetraethylammonium Iodide in Formamid.

V.	Molecular conductivity.			Dissociation.		
	15°	25°	35°	15°	25°	35°
2	11.78	15.42	19.47	62.6	63.5	64.0
4	13.86	18.10	22.78	73.7	74.5	74.0
10	15.74	20.31	25.31	83.7	83.6	83.2
50	17.60	22.69	28.47	93.6	93.5	93.6
100	18.45	23.79	29.85	98.1	98.0	98.1
200	18.81	24.28	30.43	100.0	100.0	100.0
K	2.47×10^{-5}	3.17×10^{-5}	3.94×10^{-5}			

Viscosity and Fluidity.

V.	η 15°	η 25°	η 35°	ϕ 15°	ϕ 25°	ϕ 35°
2	0.04879	0.03618	0.02802	20.50	27.64	35.68
4	0.04573	0.03486	0.02687	21.87	28.69	37.22
10	0.04431	0.03336	0.02607	22.57	29.98	38.36
Solv.	0.04284	0.03256	0.02561	23.34	30.71	39.05

TABLE XIII.—Rubidium Chloride in Formamid.

V.	Molecular conductivity.			Dissociation.		
	15°	25°	35°	15°	25°	35°
2	14.28	18.46	23.10	67.7	68.1	68.6
4	16.31	21.00	26.17	77.3	77.5	78.0
10	18.77	24.09	30.10	89.0	88.9	89.3
50	19.84	25.54	31.82	94.1	94.3	94.4
100	20.59	26.49	33.03	97.6	97.8	98.0
200	21.09	27.08	33.69	100.0	100.0	100.0
K	2.47×10^{-5}	3.17×10^{-5}	3.94×10^{-5}			

Viscosity and Fluidity.

V.	η 15°	η 25°	η 35°	ϕ 15°	ϕ 25°	ϕ 35°
2	0.05246	0.03869	0.02961	19.06	25.85	33.77
4	0.04773	0.03606	0.02778	20.95	27.73	36.00
10	0.04486	0.03396	0.02623	22.29	29.45	38.12
Solv.	0.04284	0.03256	0.02561	23.34	30.71	39.05

TABLE XIV.—Rubidium Bromide in Formamid.

V.	Molecular conductivity.			Dissociation.		
	15°	25°	35°	15°	25°	35°
4	16.36	21.26	26.52	79.8	81.1	81.2
10	18.47	23.79	29.63	90.1	90.8	90.7
50	20.49	26.21	32.68	100.0	100.0	100.0
100	20.36	26.27	32.71			
K	4.79×10^{-5}	6.07×10^{-5}	7.62×10^{-5}			

Viscosity and Fluidity.

V.	η 15°	η 25°	η 35°	ϕ 15°	ϕ 25°	ϕ 35°
2	Solution supersaturated at 25°					
4	0.04661	0.03501	0.02717	21.46	28.56	36.81
10	0.04462	0.03394	0.02648	22.41	29.46	37.76
Solv.	0.04312	0.03260	0.02564	23.19	30.68	39.00

TABLE XV.—Rubidium Iodide in Formamid.

V.	Molecular conductivity.			Dissociation.		
	15°	25°	35°	15°	25°	35°
2	14.73	19.01	23.78	72.4	72.0	72.2
4	16.87	21.71	27.21	82.9	82.2	82.6
10	18.60	24.00	29.83	91.4	90.9	90.5
50	19.59	25.27	31.49	96.3	95.7	95.6
100	20.23	26.06	32.62	99.5	98.7	98.7
200	20.34	26.41	32.95	100.0	100.0	100.0
K	3.68×10^{-5}	4.71×10^{-5}	5.87×10^{-5}			

Viscosity and Fluidity.

V.	η 15°	η 25°	η 35°	ϕ 15°	ϕ 25°	ϕ 35°
2	0.04945	0.03516	0.02865	20.22	27.66	34.90
4	0.04643	0.03503	0.02737	21.54	28.55	36.54
10	0.04432	0.03348	0.02634	22.56	29.87	37.97
Solv.	0.04201	0.03207	0.02496	23.80	31.18	40.06

The hypothesis of Dutoit and Aston (*Comptes Rendus*, 1897, cxxvii., 240) states that the greater the association factor of the solvent the greater its dissociating powers. Table 1. shows the relation of formamid to other pure solvents in regard to association factors. The correction and comparisons made above, with reference to the Thomson-Nernst theory, are equally applicable in connection with the Dutoit and Aston theory. Having these two theories in mind, it is of interest to give here the percentage dissociations of a few salts in ethyl alcohol, for comparison with the data given in Tables VII., VIII., and XIX.

Solutions in Ethyl Alcohol at 25°.

Salt.	V for—	a.
KI.. ..	8192	76.7
KCNS	6400	93.8
LiNO ₃	6400	89.9

The above table was taken from the data of Jones and Kreider. Jones and Mabin showed that complete dissociation of lithium nitrate in acetone is not reached even when V is 100,000. The significance of these figures is apparent if one has in mind the association factors and dielectric constants of formamid, ethyl alcohol, and acetone given in Table II.

Jones and Veazey's (*Am. Chem. Journ.*, 1907, xxxvii., 405; *Publication No. 80*, 1907, Carnegie Institute of Washington) explanation of the decrease in viscosity produced to the greatest extent by caesium and rubidium salts, and in a less degree by potassium, ammonium, and other salts, all having very large molecular and atomic volumes, has been of special interest in this investigation. They base their hypothesis on the theory of Thorpe and Roger, that viscosity is due to the friction between the surfaces of the molecules. If the particles of the solute are larger than those of the solvent the frictional surfaces and, consequently, the viscosity will be decreased. If the added particles are smaller than those of the solvent the viscosity will be increased by the addition of the solute. The viscosity of all the concentrated solutions of salts having very large atomic or molecular volumes has been found to be less than the solvent in the case of all pure solvents, except acetone, which have previously been studied. The viscosity of formamid has, on the contrary, been increased by every salt used. The complex formamid molecule, HCONH₂, and its very large association factor, 6.18, show that its actual molecule is larger than that of any other pure solvent used in these investigations, and the increase in viscosity by the salts named above confirms this conclusion. The following comparison strikingly illustrates this relation:—A N/2 solution of rubidium iodide in glycerol decreases the viscosity of the solvent 13 per cent, while a N/2 solution of the same salt in formamid increases the viscosity of the solvent 12.7 per cent. This relation will be referred to again in discussing the results of the work with caesium nitrate and chloride.

That the percentage temperature coefficients of conductivity increase as the viscosity of the solution increases, is a relation that has been brought out by all the investigations in this laboratory. These coefficients for solution in formamid have the order of magnitude that would be expected from the relation of their viscosities to the viscosities of the same solutions in other solvents. For example, compare the coefficients for solutions of potassium iodide in water, given in the table, with those for the same salt in formamid in Table VII.

All salts containing water of crystallisation were carefully dehydrated at suitable temperatures, just before the solutions were prepared. No thermal measurements were made of the heat of solution, but in the case of sodium iodide, which crystallises with two molecules of water, a marked rise in temperature was noted when the salt dissolved in formamid, which indicated the formation of a solvate. It is well known that solvated salts give higher temperature percentage coefficients of conductivity than non-solvated, because complexes are usually simplified by

rise in temperature. In the present investigation salts crystallising with water have given the larger coefficients, indicating the formation of solvates analogous to the formation of solvates by the same salts in water and other solvents. To illustrate this relation let us compare these coefficients for sodium chromate, crystallising with ten molecules of water (Table V.), and cobalt bromide, crystallising with two molecules of water (Table XXII.); also compare sodium iodide, crystallising with two molecules of water (Table IV.), with potassium iodide (Table VII.). The coefficients for the dilute solutions of sodium chromate are probably not reliable for this comparison, as will be explained under the discussion of this salt.

(To be continued).

THE THERMAL DECOMPOSITION OF HYDROGEN PEROXIDE IN AQUEOUS SOLUTION.*

(PRELIMINARY NOTE).

By WILLIAM CLAYTON.

WHILST the photochemical decomposition of hydrogen peroxide has been investigated in some detail (most recently by Matthews and Curtis, *Journ. Phys. Chem.*, 1914, xviii., 166, 521), the thermal decomposition, on the other hand, has received relatively little attention. The ultimate object of the present work was to investigate the latter with the object of bringing it into relation, if possible, with the photo-chemical. This was considered to be of special importance from the standpoint of homogeneous catalysis in view of the conclusions reached by Matthews and Curtis (*loc. cit.*), the chief of which are:—

(1) The photolysis of hydrogen peroxide proceeds smoothly at constant temperature and illumination, following the course of a monomolecular reaction. The reaction ceases abruptly upon extinguishing the light.

(2) The temperature coefficient of the light reaction is 1.5 approx.

(3) The same catalysts do not affect the thermal and photochemical decomposition of hydrogen peroxide in the same way. Thus the authors state that caustic soda inhibits the photochemical whilst it accelerates the thermal decomposition.

Practically all the research on the thermal decomposition of hydrogen peroxide deals not with the pure water case, but with aqueous solutions containing alkalis, salts, catalytic metals, and conserving agents. The only attempt at a complete investigation of the thermal decomposition in pure water is that of Lemoine (*Journ. Chem. Phys.*, 1914, xii., 12), who sought to determine how the velocity of the reaction varied with temperature and concentration. Lemoine concluded that the reaction was truly monomolecular, and that the temperature coefficient was from 2 to 3. Great discrepancies, however, are exhibited in the lists of constants for any given initial concentration of solution at a given temperature.

The following are a few of Lemoine's results:—

H ₂ O ₂ per cent.	Temp. °C.	Values of K, the monomolecular constant.						
98	100	1.46	3.38	3.80	—	—	—	—
57	100	3.56	2.83	7.96	2.85	1.71	—	—
56.5	100	4.39	1.95	6.03	6.42	6.11	1.60	—

Lemoine concluded that the state of the surface of the containing vessel is the most important factor. This conclusion is discussed later in the light of the results communicated in the present paper.

Although an initial period of induction (real or apparent) is not known in the photochemical decomposition (Matthews and Curtis, *loc. cit.*), Lemoine observed a

period of induction, "une certaine inertie au début," for the thermal reaction in concentrated solutions, especially at fairly low temperatures, the evolution of oxygen being inhibited for a time. He gives the following data:—

Temperature. °C.	H ₂ O ₂ . Per cent.	Period of inertia. Hrs. Mins.	
35.5	84.6	6	6
36.0	86.0	2	0
36.0	72.5	1	5
36.0	66.0	1	37
36.0	64.0	5	8

Similar induction periods have been observed in certain instances in the present work, though the solutions were dilute and the temperature relatively high. Thus a solution (1.5 per cent H₂O₂) at 60° C. showed no change in strength for five hours. A similar solution remained unchanged for nearly four hours. In another case in which the 1.5 per cent H₂O₂ solution (at 50° C.) contained NaOH (0.003 N) an induction period of at least eight hours was observed. Whether such effects are really characteristic of the reaction itself, or depend upon accidental impurity or the state of the walls of the vessel, cannot at this stage be definitely stated.

Experimental Methods and Results.

The material employed was Merck's perhydrol, diluted to the required amount. The rate of decomposition was determined by pipetting out certain quantities of the solution and titrating with N/10 KMnO₄ in H₂SO₄ solution. The decomposing solutions were placed in various flasks (Jena glass, wax-lined flasks, and quartz) suspended in electrically controlled thermostats at 50° C. and 60° C. respectively. The withdrawal of aliquot portions was carried out by means of a special pipette designed to avoid the difficulty of reading when rapid gas evolution occurred (*cf.* Walton and Judd, *Zeit. Phys. Chem.*, 1913, lxxxiii., 315).

The velocity constant of decomposition was calculated by the usual monomolecular expression—

$$K = \frac{1}{t} \log \frac{a}{a-x};$$

the values of K being obtained directly from the experimental numbers by employing logarithms to the base 10. The reaction is treated (in this preliminary investigation at any rate) as monomolecular because of the simple type of reaction involved, and also because of the fact that hydrogen peroxide in aqueous solutions is known to exist in an unpolymerised state (*cf.* Carrara, *Zeit. Phys. Chem.*, 1893, xii., 498; Orndoff and White, *Ibid.*, 1893, xii., 431; Tammann, *Ibid.*, 1893, xii., 63). In view, however, of the discrepancies observed in the values of the "constant," other "constants" were calculated, viz., that corresponding to a zero-molecular reaction $dx/dt=k$, and that corresponding to a bimolecular reaction. These values afforded no better agreement. Lemoine (*loc. cit.*) also concluded that the bimolecular equation did not hold.

As an illustration of what may be regarded as a relatively concordant set of values, two experiments carried out at 50° C. in a quartz flask containing conductivity water may be cited.

Initial concentration of H₂O₂ = 1.5 per cent.

Time (mins.).	a-x.	K (monomolecular).
0	42.4	—
95	41.5	0.000100
1199	33.4	0.000086
2657	25.0	86
2976	23.5	86
4114	18.3	88
4230	18.0	88

The same experiment was repeated in a second quartz flask, painted black on the outside to avoid photochemical effects.

* A Paper read before the Faraday Society, October 19, 1915.

L.	a-s.	K.
0	43°0	—
231	40°9	0°000943
1357	30°9	0°0001057
1597	28°9	0°0001080
2757	21°5	1092
3040	20°05	1090
3292	18°75	1095
4182	14°90	1100
5688	10°10	1106
6012	9°30	1106
7093	7°10	1102
9958	3°40	1106
Mean		0°0001093

Later results with alkaline solutions of hydrogen peroxide showed much greater variations, as also did measurements in conductivity water at 60° C. The research therefore resolved itself into a search for the possible cause or causes of these variations.

At the temperatures 50° to 60° C. the possible volatility of H₂O₂ has to be considered. It was tested for as follows:—A flask containing the H₂O₂ solution was suspended in a thermostat at 50° C., and by means of a puff-ball the gases above the solution could be swept out of the flask and made to pass into a very dilute acid solution of KMnO₄. The gases were swept out at intervals for two days. Not the slightest trace of H₂O₂ could be detected. A repetition of this experiment at 60° C. confirmed the result, and it was therefore concluded that the discrepancies could not be due to this cause. (As further evidence for the involatility of H₂O₂ at the temperatures mentioned, compare Nernst, *Zeit. Elektrochem.*, 1905, xi., 710).

Possible loss of water-vapour was prevented by closing the flasks with long air-cooled glass tubes, serving as condensers. Later, in order to avoid the possibility of dust entering the solutions and so catalysing the reaction, wax-lined tin caps, loosely fitting, were provided for the various flasks.

An interesting question also arises as to whether stirring the solutions would influence the rate of decomposition. Lemoine (*loc. cit.*) has concluded that no appreciable influence manifested itself if the solutions were agitated, if the pressure were altered, or if dust-free gases (O₂ and H₂) were bubbled through the solutions. Several stirring experiments were therefore carried out using a glass stirrer rotating moderately fast; the conclusion reached being that stirring has no appreciable effect upon the rate, at least within the limits of the experimental measurements.

(To be continued).

THE USE OF COPPER SULPHATE IN THE PURIFICATION OF SWIMMING POOLS.

By STANLEY JUDSON THOMAS.

WITHIN the past two or three years numerous articles have been written relating to the sanitary conditions of indoor swimming pools. Studies have been made by Dr. William J. Lyster at the University of Pennsylvania, Dr. M. P. Ravenel, of the University of Wisconsin, and by various other workers throughout our eastern colleges and universities. One fact is emphasised by all these authorities—that the danger of transmission of zymotic disease through the swimming pool is real. It is easy to see how a person suffering from walking typhoid may infect the limited amount of water in the pool, and thus transfer the disease to many bathers, who consciously or unconsciously take the water into their mouths. This is but an example. We might carry it further and show how readily diphtheria, cholera, skin diseases, colds, and, in fact, almost any of our bacterial diseases, may be contracted through this medium. It is not my intention to go into the subject of

the general care and upkeep of a pool. The *American Physical Education Review* of December, 1912, and February, 1913, has several excellent articles in this connection. The fact is indisputable that, besides such general precautions as preliminary bathing with soap, inspection of the bather, and rejection of dirty bathing suits, &c., some chemical treatment of the water is necessary to safeguard the health of the bathers. What this chemical shall be is the question I shall attempt to answer.

Excellent articles have been written by Dr. Ravenel ("The Hygiene of Swimming Pools," Sixth Congress of the American School Hygiene Association), Mr. S. C. Markley ("The Use of Chloride of Lime in the Purification of Swimming Pools," *Am. Phys. Educ. Rev.*, viii., 2), and others, recommending hypochlorite of lime as the disinfectant. As a precautionary treatment of public water supplies, there is no doubt that this chemical is without a peer. Innumerable examples could be given to show its efficacy. But it must be borne in mind that in the treatment of a public water supply more than 2 parts per million of "hypochlorite" is seldom necessary. This means about 0.6 part per million of available chlorine. When this maximum amount is used aeration of the water is necessary to remove the disagreeable odour and taste of the "hypochlorite." Now consider the use of this chemical in a swimming pool. Dr. Ravenel found that 1 part per million of available chlorine was necessary to sterilise the water. That means 3 parts per million of the hypochlorite, and as the usual method proposed is to dissolve the salt in the pool directly one can imagine the unpleasant odour and taste of the water. "Aeration" is effected, it is true, but "aeration" only releases the odour from the water into the enclosed room surrounding the pool.

The use of 2.5 parts per million "hypochlorite" was tried in the Taylor Gymnasium pool, at Lehigh University, and even at this dilution the odour was marked. That the treatment was not effective is shown by the results of the bacteriological analyses of the pool during the treatment (Table I.).

TABLE I.—Bacteriological Examination of Taylor Gymnasium Swimming Pool.

Day and Time, November, 1914.	Count per cc. Gelatin. Agar.		B. coli, per cc.
8 12.00 m.	50	10	0 (a)
9 9.00 a.m.	200	1400	0 (b)
10 10.30 a.m.	2700	1500	50
10 11.15 a.m.	3000	5300	200 (c)
10 2.00 p.m.	2	5	0 (d)
10 5.45 p.m.	50	800	0
11 3.00 p.m.	400	1000	340
12 5.00 p.m.	800	3000	400
13 2.30 p.m.	100	500	100 (e)
13 2.45 p.m.	0	3	0 (f)
14 5.00 p.m.	50	400	10

- (a) Fresh water.
- (b) Three men had been in the pool.
- (c) Forty men in pool since last sample.
- (d) 2.5 parts per million hypochlorite added at 11.30 a.m. No one in pool since 11.15.
- (e) 3000 gallons fresh water added.
- (f) Sample taken after 2.5 parts per million hypochlorite were added.

From these results it may be seen that, though 2.5 parts per million of hypochlorite of lime purifies the water shortly after its introduction into the pool, it soon loses its germicidal properties, and is unable to destroy the bacteria which are constantly being brought in by new bathers. To add 2.5 parts per million of the "hypochlorite" every day would probably solve the problem from a bacteriological standpoint, but the odour would be too offensive for this form of treatment to be considered.

This pool is equipped with a double unit mechanical filter in which alum is used as a coagulant. By this refiltration system the water is always kept clear. The bacterial content of the pool cannot be kept low, however, by this treatment alone. The idea was conceived, and acted upon, of using a small amount of copper sulphate in connection with the alum treatment, not, however, by mixing the copper sulphate with the alum, but by introducing it directly into the pool after the completion of the alum coagulation, which removes the carbonates and bicarbonates that would otherwise hinder the action of the copper sulphate. The result of using 0.4 part per million of copper sulphate proved to be very satisfactory, as will be shown later.

I shall now discuss the use of copper sulphate as a germicide, and attempt to show its advantage over hypochlorite of lime as a disinfectant of swimming pools.

In a paper written in the early eighties, Carl von Naegeli ("Ueber Oligodynamische Erscheinungen in Lebenden Zellen"), one of the greatest German botanists of the past century, showed how exceedingly sensitive certain living plants are to minute quantities of various metals. He found that certain spirogyra are unable to resist the toxic effect of one part of copper to one thousand million parts of water, and that minute quantities of other metals, such as silver, lead, tin, iron, and mercury, manifested "oligodynamic" properties. ("Oligodynamic"—derived from two Greek words meaning the force within a small quantity of a substance). Israel and Klingmann ("Oligodynamische Erscheinungen—v. Naegeli—an Pflanzlichen und Thierischen Zellen," *Virchow's Archiv.*, 1897, pp. 293—340), in 1897, studied the effect of copper on certain bacteria, spirogyra, and animal forms. Bacteria and spirogyra were very sensitive, and were easily killed with dilute solutions. In the case of the animal forms, while the toxic effects were visible in most cases with dilute solutions, vorticella and a few others require a larger amount of the metal. Locke found that traces of copper contained in water distilled in copper vessels were sufficient to destroy tubifex (one of the annelid worms) and tadpoles. Cushing, in 1899, gave a good description of the work done up to that time along this line ("Pharmacology and Therapeutics," 1899, p. 159).

The fact that these discoveries were of great economic importance was first brought out by Dr. George T. Moore, of the U.S. Department of Agriculture. In 1904 the U.S. Department of Agriculture, Bureau of Plant Industry, published the results of Dr. Moore's experiments with copper sulphate as an algicide and disinfectant in polluted water ("A Method of Destroying or Preventing the Growth of Algæ and certain Pathogenic Bacteria in Water Supplies," by Moore and Kellermann, U.S. Department of Agriculture, Bureau of Plant Industry, *Bull.* 64). In that paper it was recommended that copper sulphate be used in the dilution of one part to one thousand parts of water. In December of the same year, the *American Journal of Pharmacy* (1904, lxxvii, 553) published an article by Dr. Moore ("A New Method for the Purification of Water Supplies," an Address given before the American Philosophical Society, Oct. 21, 1904), and one by Dr. Henry Kraemer ("The Copper Treatment of Water," *Am. Journ. Pharm.*, 1904, lxxvii, 574), of the Philadelphia College of Pharmacy. In his paper, Dr. Moore reviewed thoroughly the practical application of copper sulphate in municipal water supplies, chiefly as an algicide. The first reservoir so treated was that of the Winchester Water Co. at Winchester, Ky. The success of the treatment is best given in Dr. Moore's own words:—

"In June, 1903, our attention was called to the condition of the reservoir at Winchester, Ky. This supply was constructed in 1890, and after the first three years a strong odour and taste were noticeable in the water during the hot summer months. This condition gradually increased until the water attained such a degree of offensiveness as to make its use for any purpose almost intolerable. Aeration and mechanical filtration were tried without effect,

and it seemed that the only hope for relief was to abandon the entire reservoir and go ten miles to the Kentucky River for the source of a new supply. The cost, however, was too great to be considered, and for this reason the difficulty was considerably increased. A microscopical examination of the water showed that the odour and taste were due to the presence of one of the blue-green algæ, and it was believed that the application of copper sulphate at the rate of about 1 to 5,000,000 would be sufficient to destroy these forms; consequently, there being no objection on the part of either the water board or the health authorities, a treatment was made, and the results have been everything that could be desired. Within three or four days the odour disappeared and the water was perfectly clear. This summer at about the same time it was feared that the algal growth was reappearing, and for this reason another slight treatment was made, but with this exception no copper has been added to the water since the original treatment in June, 1903, and it has remained perfectly clean and sweet."

After citing numerous other examples of the efficiency of copper sulphate as an algicide Dr. Moore says:—"Very naturally after it was noted that the algæ were so susceptible to infinitesimal quantities of copper, it seemed worth while to test the effect of this metal upon typhoid and cholera germs, these being the two pathogenic forms which are most commonly conveyed by water. As the result of some 500 or 600 experiments it was demonstrated that, while these bacteria were not as sensitive as the algæ, still the dilution necessary to produce death was sufficiently great to warrant the belief that under certain conditions efficient sterilisation of large bodies of water could be brought about."

Dr. Kraemer, in corroborating Dr. Moore's results, goes further into the effect of copper sulphate on the human system. He points out that the salt was most beneficial in removing algæ from watercress beds, while not harming the cress, and adds:—"It seems to me that this is in a measure due to the fact that in the algæ the entire individual is comprised in a single cell, which performs all the vegetable as well as the reproductive functions, and being entirely surrounded by the water containing the copper sulphate, all the life processes of the plant are affected, there being no way for it to distribute the solution to other cells, and thus by a dilution minimise the toxic action of the copper." Dr. Kraemer allowed copper foil to dissolve in water in conducting his experiments. While this has the toxic power of the sulphate it has not its added power of sedimentation. His results are conclusive in showing that the intestinal bacteria like colon and typhoid are completely destroyed by placing clean copper foil in the water containing them.

Mr. Alfred M. Quick, in 1904, gave the results of the use of copper sulphate in Lake Clifton of the Baltimore Waterworks ("The Use of Copper Sulphate in Lake Clifton," *Eng. News*, lii., 284). On July 28, *B. coli* were present in 1 cc. of the water. The next day copper sulphate in the dilution of 1:6,390,000 was used. On August 3, analysis showed *B. coli* absent. James M. Caird showed the results of the use of 1½ parts per million of copper sulphate in the water supply of Elmira, N.Y. ("Purification of the Water Supply at Elmira, N.Y.," *Eng. News*, lii., 34). On June 24, analysis showed *B. coli* 2 per cc., and the total count was 315 per cc. On June 30, after treatment, *B. coli* were absent, and the total count was 18 per cc.

In April, 1905, Moore and Kellerman supplemented Dr. Moore's previous article, and gave a complete description of all phases of the question. (See "Copper as an Algicide and Disinfectant in Water Supplies," *Bull.* 76 U.S. Dept. of Agriculture, Bureau of Plant Industry). Numerous reports from cities upon the effect of the treatment are given. Notable among these is one from Columbus, Ohio. A badly polluted water supply had caused for over a year an almost continuous epidemic of typhoid fever. The copper sulphate treatment was

resorted to, but later discontinued "after the daily papers published glaring accounts of the danger attendant upon such treatment." A tabulation of the data shows clearly the results of the use and non-use of copper sulphate. The salt was used in the dilution of 1 part in 1,500,000.

	Month.	Typhoid cases reported.
No copper used	June	24
No copper used	July	33
Copper used after 19th. . .	August	52
Copper used	September	16
Copper used	October	16
Copper used	November	8
Copper used	December	4 (a)
Copper discontinued after 5th	January	91
No copper used	February	376
No copper used	To March 27th	279

(a) Seventeen cases were reported, but only four were users of city water.

The chief objections to the use of copper sulphate were based on the fact that it *might* be harmful to man. Aside from the puerile charges against it that have been made by certain ignorant advertisers a few doctors maintained that nothing was known of the effect of continued use of the salt. It would be impossible even to refer to most of the literature that has been published relating to the harmlessness of this treatment. Dr. Moore and Dr. Kraemer have both collected statements from the leading toxicologists in this and many foreign countries which answer fully all objections.

Dr. Henry Kraemer published an article in 1905, showing the amounts of metallic copper normally contained in over a hundred foods ("The Use of Copper in Destroying Typhoid Organisms and the Effects of Copper on Man," *Am. Journ. Pharm.*, lxxvii., 6). If these foods can be eaten with impunity, it may be easily seen what slight chance there is of being poisoned by the small amount of copper we use for water purification. Dr. Kraemer's results, Table II., show the quantities of copper in mgrms. found in a kgrm. of the foods, which corresponds to parts per million in a tabulation of the results obtained in its use in water. As metallic copper comprises only 25 per cent of copper sulphate these results must be quadrupled if an exact comparison is to be made.

TABLE II.—Quantity of Metallic Copper in mgrms. per kgrm. of Various Foods.

Almonds (15)	36.8
Apricots (15)	1.0
Cherries (15)	2.3
Cocoa, pure, no husks (18) ..	47.0
Cucumbers (15)	45.0
Egg, yolk (11)	5.6
Egg, white (11)	7.2
Figs (15)	15.1
Grapes, Catawba (19)	1.01
Kidney, beef (12)	4.0
Milk, cow (12)	1.6
Oatmeal (19)	4.27
Peas, French (7)	59.4
Potatoes (5)	2.8
Strawberries (15)	8.0

Add to this the statements of many eminent physicians (Dr. Lucien F. Salomon, *New Orleans Medical and Surgical Journal*, June, 1902) relating to the beneficial effects of copper as a curative measure for typhoid fever and cholera, and the exhaustive study made by Dr. Walker, of London ("The Prophylactic Power of Copper in Epidemic Cholera"), and our case seems to be complete. Dr. Burg, of Paris, visited or corresponded with every important copper mine and foundry in Europe where workmen could possibly become impregnated with copper. The results of his study lead to the following conclusion:

which he addressed to the Academy of Medicine and Sciences:—

"1. Complete immunity from cholera of the immense majority of all workmen whose calling necessitates their being habitually in contact with copper dust.

"2. Copper and its alloys, brass and bronze, permanently applied to large surfaces of the common integument, are a most precious preventative, which ought in no wise to be neglected, and can cause no inconvenience. If these means leave something to be desired as a prophylactic, it will probably be found expedient to reduce the metal to an impalpable powder and to ingest a few pinches.

"3. In the treatment of cholera, copper, opportunely administered, whether in copper filing alone or in any other form which experience shall determine, affords the greatest probability of proving in the hands of the physician a powerful means of cure."

Having been convinced that even in fairly large doses copper sulphate is harmless to the human system, I tried its germicidal effect in the Taylor Gymnasium pool. As the pool water at the time was being re filtered daily, a small amount of alum being added to aid the mechanical filter—I took the opportunity of first determining the efficiency of the alum treatment. As the copper treatment immediately followed the alum treatment, I have tabulated my results together.

Table III. shows the results of the use of alum and of alum and copper sulphate.

TABLE III.—Bacteriological Examination of Taylor Gymnasium Swimming Pool.

Date, 1914	Gelatin count per cc.	<i>B. coli</i> per cc.	Additions.
5/11	4	0	
11	790	7	
12	9,000	180	
13	18,000	100	
14	48,000	90	1.0 part per million alum per day.
15	16,500	250	
16	6,900	400	
17	36,000	400	
18	4,800	29	22,000 gallons fresh water.
19	10,000	200	
5/20	8,000	1000	
21	6,000	50	1.0 part per million alum per day.
22	18,000	100	
23	30,000	150	
24	9,000	80	
25	27,000	300	
26	5,000	5	
27	2,500	0	
28	100	0	
29	2,000	4	0.04 part per million CuSO ₄ per day.
30	500	0	
6/2	5,000	9	
3	6,000	14	
Average per week.			
1st Alum treatment	15,000	390	
2nd 2.5 part per million "hydrochlorite" ..	1,500	148	
3rd 0.4 part per million CuSO ₄	3,014	5	

Although copper sulphate is slightly more expensive than hypochlorite of lime, about 1.00 dol. per hundredweight, it is effective in much smaller quantities and hence is cheaper to use.

The germicidal action of the copper sulphate is probably that of a crystalloid, permeating the cell wall and thereby producing the toxic effects.

In the presence of the bicarbonate of magnesium and calcium the following reaction takes place:—
 $\text{CuSO}_4 + \text{Ca}(\text{HCO}_3)_2 = \text{CaSO}_4 + \text{Cu}(\text{OH})_2 + 2\text{CO}_2$

This chemical change, while it destroys the toxic power of the salt, really aids in the ultimate purification of the water, since the hydroxide formed acts as a coagulant uniting with the suspended organic matter.

Summary.

The advantages of copper sulphate over hypochlorite of as a disinfectant for swimming pools, therefore, may be summarised as follows:—

I. It is more effective because it does not undergo chemical change readily. Hypochlorite owes its power to the chemical change, and is afterwards useless.

II. It is not irritating to the eyes and mucous membranes as is "hypochlorite" if the latter is used in germicidal quantities.

III. It is cheaper.

IV. It has no odour. If all other conditions were equal this last fact alone would prove its great advantage over "hypochlorite."—*Journal of Industrial and Engineering Chemistry*, vii., No. 6.

RESEARCH AND PROGRESS IN AMERICAN MANUFACTURE.*

WHAT THE INVESTIGATOR HAS DONE AND CAN DO FOR INDUSTRIES.

By Dr. RAYMOND F. BACON, of the Mellon Institute of the University of Pittsburgh.

(Concluded from p. 302).

The Manufacture of Nitric Acid.

THE manufacture of nitric acid, first begun in this country about 1834, was advanced by the form of apparatus devised by the chemist, Hart, and received its first great impetus about 1862, when the commercial manufacture of nitroglycerin began. It has later derived much nourishment from the great celluloid and nitro-cellulose industries, also indissolubly linked with the work of the research chemist. Nitroglycerin, dynamite, gun-cotton, pyroxylin varnishes, plastics and powders, photographic films, and artificial silk, are all the result of a line of concerted research activity.

In this connection, it is appropriate to refer to an accomplishment of electro-chemical research, which has demonstrably multiplied the food-supply sources of all civilised countries—the process, laboriously wrought, of effecting the combination of the nitrogen and oxygen of the air, and thus producing nitric acid and its salts. The great adaptability of certain parts of our country to electro-chemical manufacturing on account of the water-power available, may soon introduce this air-fertiliser industry.

The Electro-chemical Industries.

The application of electrical energy has greatly facilitated the work of the industrial researcher, who has thus been enabled to perform easily some very difficult operations, and in some cases to accomplish results which would be otherwise impossible.

The electrolytic alkali industry is barely twenty-five years old, yet it has largely superseded the older chemical process for the production of caustic soda from common salt. Chlorates and perchlorates are now made by electrolysis. Metallic sodium may be produced at one-fourth the cost of making it by any chemical method. Magnesium cannot be practically manufactured by other than the electrolytic process. Aluminium can not be produced for less than 1 dol. per pound by purely chemical methods; but electro-chemistry enables the manufacturers to sell it at one-fourth this cost. This metal is one of the most important next to iron and steel, and 72,379,000 lbs. of it were produced by one American company in 1913. Copper, lead, silver, and gold are now refined by electrolysis; in fact, the total electrolytic production of copper amounted to 1,629,930,359 lbs. in 1913.

* Address delivered at the National Exposition of Chemical Industries, Grand Central Palace, New York, September 25, 1915. From the *Scientific American Supplement*, No. 2081.

Among other commercial products of importance, artificial graphite, carborundum, alundum, silicon, calcium carbide, cyanamide, titanium, boron, phosphorus, and carbon disulphide are all made electrochemically by processes which were worked out by research. Electric furnace pig-iron and electric steel are now made and sold at a profit; the development of these manufactures is calling for the best efforts of electrometallurgical research, and it is reported that the United States Steel Corporation has expended over 800,000 dols. in investigations on the electrothermic production of steel.

The Glass Industry.

The production of glass, which reached a high state of development in olden times through pure empiricism, has greatly benefited by chemical research, although the contributions of the chemist to this industry are obscured by the epoch-making developments in methods of mechanical manipulation (working and handling the molten glass) effected by another industrial researcher, the experimental mechanical engineer. As I have indicated in another place, the glass industrialist has many problems (*Fourn. Ind. Eng. Chem.*, 1915, vii., 335), but his troubles will vanish when the chemical constitution of glass is definitely determined, when the ideal non-contaminating pot or tank is found, and when heat is better utilised. (Only 5 per cent is actually utilised in making glass).

The Fertiliser Industry.

Research has played a most important part in the development of the various industries which are dependent upon the products of the soil. No service has, however, been of such constructive value to agriculture as the chemical research which has eventuated in the great fertiliser industry of to-day.

The necessity of the fertiliser industry was indicated by Justus von Liebig, who in 1840, after exhaustive investigations, enunciated the foundation principles of modern agricultural chemistry, and the conclusion of this savant, that one must restore to the soil that which the removal of the crop has withdrawn if one would prevent its exhaustion, is the basis of agricultural practice to-day. The production of superphosphate followed Liebig's researches in 1842, since which time the process of manufacture has been gradually developed until the insoluble phosphoric acid is only a fraction of 1 per cent, and we have a double superphosphate, containing from 45 to 50 per cent of available phosphoric acid. Research has also solved the recovery of nitrogen from waste gases; it has made material progress toward converting the nitrogen of the air into forms suitable for plant nutrition, and has shown that it is possible to convert many waste products into fertiliser materials. These are merely some of the accomplishments of research for an industry which is the backbone of agriculture, the foundation of industry.

(NOTE.—It may be noted here that not only was Baltimore the principal market for fertilisers until some time after the Civil War, but it was also the centre of chemical fertiliser research from the beginning of the artificial fertiliser industry in 1850, when spent bone-black from the sugar refineries was first utilised and superphosphate first manufactured, until 1855, when Peruvian guano became so popular).

I beg to remind you in this place of a potent factor in our agricultural, and hence industrial, growth—the experiment stations established by the Government in the various States. All of these stations are in charge of efficient specialists, and many intricate problems of national importance have been solved.

The Cottonseed Oil Industry.

In the great cottonseed oil industry (4,767,800 tons of seed were crushed in 1913), Wesson has reported (*Fourn. Ind. Eng. Chem.*, 1915, vii., 277) that while the chemist has worked to improve the manufacturing side of the industry he has been the means of putting something like

125,000,000 dols. every year in the hands of the farmers. Among other things, chemical research has rendered service to this industry by putting the refining of the crude oil on a more rational basis, by preventing losses in manufacture, and by devising the hydrogenation process, whereby wholesome edible fats of the consistency of butter are now being produced from our cheapest vegetable oil.

The Corn Products Industry.

In a notable address on "Efficiency in Chemical Industries" T. B. Wagner has shown that the corn products industry furnishes one of the most striking examples of what efficiency has done for the development of a chemical industry within a comparatively brief space of time. To quote Wagner (*Trans. Am. Inst. Chem. Eng.*, 1913, vi., 1):—"We pay to-day for our raw material, corn, three times as much as did our predecessors, and yet we sell our products in the markets of the world at one-third of their price."

Research has been the making of the industry of corn products. According to President Bedford, of the Corn Products Refining Company (*Journ. Ind. Eng. Chem.*, 1915, vii., 275):—"While the chemist was most active from the very beginning in developing the process for making glucose and grape sugar and in steadily improving their quality, he also demonstrated his value to the industry by developing new staple products, such as starches for culinary and technical purposes, of dextrins and gums and various sugars, which in point of purity rival cane and beet sugar. These products are now manufactured in this country in very large quantities and are being shipped to all parts of the world. A brief reference to statistics will illustrate the effect of such work. The corn manufactured into corn products in this country amounts to 50,000,000 bushels per year. It is converted into 800,000,000 lbs. of corn syrup, 600,000,000 lbs. of starch, 230,000,000 lbs. of corn sugar, 625,000,000 lbs. of gluten feed, 75,000,000 lbs. of oil, and 90,000,000 lbs. of oil-cake."

Other Industries.

The manufactures of pulp and paper, sugar, textiles, leather, and cement are other industries based largely on chemical processes; they have, therefore, been mainly dependent upon research for their advancement.

There has been very little research activity in the destructive distillation of wood industry. As a consequence thereof this branch of manufacture has been undergoing a trying ordeal, and those engaged therein must soon avail themselves of chemistry if the many problems are to be solved. A more rational utilisation of wood-tar is essential for the future of this industry, and new uses for methyl alcohol and acetate of lime are anxiously desired. Only research can render these services by creating the needed markets.

Another manufacture which has taken little advantage of scientific research is the earthenware industry. While the technology of pottery is comparatively simple, potters could profit immensely by the extension of fostered research, and ceramic chemists would in turn greatly benefit by the opportunities thus offered. The American Ceramic Society has been active in endeavouring to arouse the interest of industrialists in this field in the value of research, but the art of pottery presents a more ancient alliance between art and utility than any other branch of manufacture, and the potter is proud of his lineage and his inherited empiricism.

At the present time a number of American plants are engaged in the manufacture of products which enter into the making of war supplies. Since these plants may at the conclusion of hostilities be converted into chemical manufacturing, a number of fields of industrial research will probably be opened up. With the profits which shall have accrued from ammunition production there will be no lack of capital in certain quarters for building up a synthetic-organic chemical industry.

Industrial Research Methods.

It must not be assumed that because an industry has been advantaged by research the manufacturers engaged therein usually make a practice of maintaining research laboratories. As a matter of fact, in the United States probably not more than 150 manufacturing establishments employ research chemists, although at least ten companies are spending over 100,000 dols. per year in research.

A number of our industrialists hold that they are able to purchase improvements in processes and plant without the risk of experimental expenses. This policy is practised to quite a large extent, but is open to the objection that the risk of not finding new developments or of not having an opportunity to purchase them may result in losses many times greater than the expense of supporting research laboratories.

Still other manufacturers either have their researches conducted in universities or scientific institutes, or combine with others for the support of investigations on problems of common interest—that is, the problems are attacked outside of the plants. Co-operation is now being brought about in a measure by the organisations represented in different industries. An unfortunately frequent difficulty encountered in the employment of research chemists or in the establishment of a research laboratory is that many manufacturers do not appear to grasp the need or importance of such work, or know how to treat the men in charge so as to secure the best results. The industrialist may not even fully understand just what is the cause of his manufacturing losses or to whom to turn for aid. If he eventually engages a chemist he is sometimes likely to regard him as a sort of master of mysteries who should be able to accomplish wonders, and if he cannot see definite results in the course of a few months is occasionally apt to consider the investment a bad one and to regard research chemists as a class as a useless lot. It has not been unusual for the chemist to be told to remain in his laboratory and not to go in or about the works, and he must also face the natural opposition of workmen to any innovations and reckon with the jealousies of foremen and of various officials.

From the standpoint of the manufacturer one decided advantage of the policy of having all problems worked out within the plant is that the results secured are not divulged, but are stored away in the laboratory archives and become part of the assets and working capital of the corporation which has paid for them, and it is usually not until patent applications are filed that this knowledge, generally only partially and imperfectly, becomes publicly known. When it is not deemed necessary to take out patents such knowledge is often permanently buried.

In this matter of the dissemination of knowledge concerning chemical practice it must be evident to all that there is but little co-operation between the manufacturers and the universities. Chemical manufacturers have been quite naturally opposed to publishing any discoveries made in their plants, since "knowledge is power" in manufacturing as elsewhere, and new knowledge gained in the laboratories of the company may often very properly be regarded as among the most valuable assets of the firm. The universities and the scientific societies, on the other hand, exist for the diffusion of knowledge, and from their standpoint the great disadvantage of the above policy is this concealment of knowledge, for it results in a serious retardation of the general growth and development of science in its broader aspects, and renders it much more difficult for the universities to train men properly for such industries, since all text-books and general knowledge available would in all probability be far behind the actual manufacturing practice. Fortunately the policy of industrial secrecy is becoming more generally regarded in the light of reason, and there is a growing inclination among manufacturers to disclose the details of investigations, which according to tradition would be carefully guarded. These manufacturers appreciate the facts that public interest in chemical achievements is stimulating to further

fruitful research, that helpful suggestions and information may come from other investigators upon the publication of any results, and that the exchange of knowledge prevents many costly repetitions.

Industrial Fellowships.

If the manufacturer elects to refer his problem to the university or technical school such reference may take the form of an industrial fellowship, and much has been and may be said in favour of these fellowships. They allow the donor to keep secret for three years the results secured, after which they may be published. They also secure to him patent rights. They give highly specialised training to properly qualified men, and often secure for them permanent positions and shares in the profits of their discoveries. It should be obvious at the outset that a fellowship of this character can be successful only when there are close confidential relations obtaining between the manufacturer and the officer in charge of the research, for no such co-operation can be really effective unless based upon a thorough mutual familiarity with the conditions and an abiding faith in the integrity and sincerity of purpose of each other. It is likely to prove a poor investment for a manufacturer to seek the aid of an investigator if he is unwilling to take such expert into his confidence and to familiarise him with all the local and other factors which enter into the problem from a manufacturing standpoint.

According to the system of industrial research in operation at the Mellon Institute of Industrial Research of the University of Pittsburgh, a manufacturer having a problem requiring solution may become the donor of a fellowship; said manufacturer provides the salary of the Fellow selected to conduct the investigation desired, the institute furnishing such facilities as are necessary for the conduct of the work. (On the object and work of the Mellon Institute, see Bacon, *Journ. Ind. Eng. Chem.*, 1915, vii., 343).

Even at the risk of appearing to secure a gratuitous advertisement for the Mellon Institute (however, this institution is not in any sense of the word of a commercial nature) I beg to present a table showing the growth of the system of industrial research in operation therein, a record of the growing appreciation by American industrialists of a form of service to manufacturing which is characterised by scientists as being both "eminently practical" (G. G. Henderson in *Journ. Soc. Chem. Ind.*, 1915, xxxiv., 751) and "admirable" (Sir William Ramsay, *ibid.*, 753):—

Academic year.	Number of fellowships in operation.	Number of Fellows.	Amounts subscribed for the maintenance of fellowships.
1911-12 ..	11	23	39,700 dols.
1912-13 ..	16	30	53,500 "
1913-14 ..	15	29	59,100 "
1914-15 ..	24	42	74,350 "

At the present time thirty fellowships are in operation, and over 175,000 dols. is being expended annually for salaries and maintenance.

Research and the National Welfare.

One of the alleviating circumstances in the disaster of the European war is the fact that it forces on the attention of all the place that science holds in national and international affairs. As Cattell observes, science does not necessarily or at once make us moral or wise, although its general influence is in this direction, for human nature cannot be greatly altered by a change in the environment effective for a short period and on some individuals, but when the new conditions become general and individuals are favoured who fit into them, so that an altered race is preserved by natural selection, science will make our morality and enforce its observance.

Those who fail to understand the argument that science will ultimately control human conduct must be convinced

by the argument of accomplished fact that science is essential to national efficiency. Germany adjusts the nation to be self-supporting and self-sufficient, because it has a better organisation of science than the other nations. That nation did not spend so much per capita on its army and navy as Great Britain or France, but it spent more on science and regarded science more highly (see Bacon, *Science*, 1914, xl., 871 *et seq.*). It has been stated that the British Government employs seventeen chemists, the German Government about one thousand. It is said with much show of reason that Germany has developed an efficient military machine by subordinating the individual to discipline from above. It is not less true that the German university has been one of the most anarchic of institutions, both students and professors having had freedom greater than they have in American universities, and at the present moment Germany owes more to its universities as they have been conducted in the past than to its army as it is now organised.

A complicated machine is not useful in order to meet an emergency, but rather the scientific attitude and the scientific training which can react to the situation. A super-dreadnought built at a cost, say, of 15,000,000 dols., may be an asset or a burden; an equal sum spent in selecting and educating 3000 scientific men would nearly double the number of men in the country competent to advance science. The dreadnought is a continual expense; it depreciates at the rate of a million dollars a year; its existence tends to exert an influence toward a war of aggression. The three thousand scientific men would add to the wealth of the country in peace, to its strength in a war of defence. If the number of men engaged in scientific research and in the application of science could be doubled, the gain would be incalculable.

The formation of the Naval Advisory Board by Secretary Daniels is distinctly an official recognition of the accomplishments of our scientists. This board is to advise the Secretary of the Navy regarding new inventions and possible methods of improving the defensive and offensive qualities of the American Navy, and the chemical profession is officially represented by two distinguished researchers, Drs. L. H. Baekeland and W. R. Whitney.

RADIUM PRODUCTION FROM COLORADO CARNOTITE ORES BY U.S. BUREAU OF MINES.

ACCORDING to an announcement of Secretary of the Interior Franklin K. Lane the production of radium from Colorado carnotite ores by the Bureau of Mines, in connection with the National Radium Institute, has passed the experimental stage in its new process, and is now on a successful manufacturing basis. He also declared that the statements made to Congress concerning the ability of the Bureau of Mines to produce radium at a greatly decreased cost over other processes had actually been accomplished, and that the costs were even less than predicted.

The cost of 1 gm. of radium metal produced in the form of bromide during March, April, and May of the present year was 36,050 dols. This includes the cost of ore, insurance, repairs, amortisation allowance for plant and equipment, cost of Bureau of Mines co-operation, and all expenses incident to the production of high-grade radium bromide. When it is considered that radium has been selling for 120,000 dols. and 160,000 dols. a gm., it will be seen just what the Bureau of Mines has accomplished along these lines.

The cost of producing radium in the small experimental plant during the first few months of the Bureau's activities was somewhat higher, but not enough to seriously affect the final average.

The public, however, should not infer that this low cost

of production necessarily means an immediate drop in the selling price of radium. The National Radium Institute was fortunate in securing through the Crucible Steel Company the right to mine ten claims of carnotite ores belonging to them, and this was practically the only ore available at the time. Since then new deposits have been opened, but these are closely held, and, according to the best judgment of the experts employed by the Bureau of Mines, the Colorado and Utah fields, which are much richer in radium-bearing ores than any others known, will supply ore for a few years only at the rate of production that obtained when the European war closed down the mines. The demand for radium will also increase rapidly, for the two or three surgeons who have a sufficient amount of this element to entitle them to speak from experience are obtaining results in the cure of cancer that are increasingly encouraging as their knowledge of its application improves. A few more reports like that presented to the American Medical Association at its recent San Francisco meeting and the medical profession as a whole will be convinced of its efficacy. Under all the circumstances that have come to my knowledge it does seem to me that it behoves the Government to make some arrangement whereby these deposits, so unique in their extent and their richness, may be conserved in the truest sense for our people, by extracting the radium from the ores where it now lies useless and putting it to work for the eradication of cancer in the hospitals of the army and navy and the public health service.

The ten carnotite claims being operated at Long Park, Colorado, by the National Radium Institute have already produced over 796 tons of ore averaging above 2 per cent uranium oxide. The cost of ore delivered at the radium plant in Denver has averaged \$1 dols. 30c. per ton. This included 15 per cent royalty, salary of Bureau of Mines employes, amortisation of camp and equipment, and all expenses incident to the mining, transportation, grinding, and sampling of the ore.

A concentrating plant for low-grade ores has been erected at the mines and is successfully recovering material formerly wasted. Grinding and sampling machinery has been installed at Denver and a radium extraction plant erected in the same city. The radium plant has now a capacity of three tons of ore per day, having been more than doubled in size since last February. Before that time the plant had been run more or less on an experimental scale, although regularly producing radium since June, 1914. To July 1 slightly over 3 grms. of radium metal had been obtained in the form of radium barium sulphate, containing over 1 mgrm. of radium to the kilogram. The conversion of the sulphates into chlorides and the purification of the radium therefrom is easily accomplished and with very small loss of material. Unfortunately, however, special acid proof enamel ware, obtainable only in France, has not been delivered of sufficient capacity to handle the crystallisation of the full plant production, so that a little less than half the output—or, to be exact, 1304 mgrms. of radium element—have been delivered to the two hospitals connected with the National Radium Institute. The radium remaining can be crystallised at any time from neutral solution to apparatus already installed, but the greater rapidity and efficiency of production of this very valuable material by the methods used have decided the Bureau of Mines to await the completion of apparatus now being built before pushing the chloride crystallisation to full capacity.

The average radium extraction of all ore mined by the National Radium Institute has been over 85 per cent of the amount present in the ore as determined by actual measurement. The amount present in the ore has been found, in fact, to be essentially the same as the theoretical amount required by the uranium-radium ratio. The extraction figures for the last five carloads of carnotite treated has shown a recovery of over 90 per cent in each case.—*Chemical Engineer*, xxii., No. 3.

NOTICES OF BOOKS.

The Gases of the Atmosphere. By Sir WILLIAM RAMSAY, K.C.B., F.R.S. Fourth Edition. London: Macmillan and Co., Ltd. 1915.

IN the fourth edition of this book an account is given of the progress made in the last ten years in the investigation of the atmosphere, especially in reference to our knowledge of niton, or radium emanation. Sir William Ramsay's experiments on the molecular weight of niton, its melting and boiling points, are described, and the question of the possible sources of the rare gases in the atmosphere is shortly discussed. The discovery of the real nature of the atmosphere forms a chapter of great interest and importance in the history of modern chemistry, and the book provides an admirable exposition of the subject.

Limes and Cements. By ERNEST A. DANCASTER, B.Sc. (Lond.). London: Crosby Lockwood and Son. 1915.

THE manufacture of different kinds of cements and the uses to which they are put are briefly described in this book, which is well adapted to be employed as an introductory text-book by students in technical colleges. Recent research, especially on Portland cement, which has led to the expansion and development of the industry, is well described, and the chemistry of Portland cement is treated comparatively fully. In the descriptions of kilns, &c., much attention is paid to Continental practice; thus French methods of plastering and also those employed in India are discussed at some length. Technical methods of analysing limes and cements, &c., are included, and the most important physical and mechanical tests are also described.

Modern Chemistry and Its Wonders. By GEOFFREY MARTIN, D.Sc., Ph.D. London: Sampson Low, Marston, and Co., Ltd. 1915.

THE author of this book has at his command an enthusiastic and inspiring flow of language, and he makes excellent use of his gift for interesting his readers even in subjects which cannot be explained without a good deal of technical language. The book is a companion volume to the author's recently published "Triumphs and Wonders of Modern Chemistry," which was heartily appreciated by the public, and was, moreover, translated into Russian. This volume will no doubt be equally well received. Some of the titles of the chapters may be quoted to indicate the scope of the book:—The Romance of Explosives, Radium and the New Chemistry, The Radio-Elements and the Periodic Law, The Romance of the Hydrocarbons, The Romance of Sugar, Metallic Firestones. The importance of recent discoveries in these and other different subjects are admirably put before the reader in a chatty and anecdotal style which is bound to interest and amuse him, and, while technical details are as far as possible avoided, scientific accuracy has not been sacrificed.

University College of North Wales: Calendar for the Session 1915-16. Weston-super-Mare: Lawrence Bros. 1915.

THE Calendar of University College of North Wales for the Session 1915-16 contains full details of the courses of work in all subjects, with list of fees and time tables. The papers of the Scholarship Examination of April, 1915, are included, and the syllabus of the Scholarship Examination of 1916. The Calendar contains the prospectuses of the departments of Agriculture, Forestry, Electrical Engineering, and Training of Elementary, Secondary, and Kindergarten School Teachers, in which the courses of study in each department are outlined. A full list of all the original papers and articles published by members of the College is included, and a short statement is made as to special military work arising out of the war.

Journal of the Association of Official Agricultural Chemists. 1915, vol. i., No. 1. Baltimore, U.S.A.: Williams and Wilkins Co.

THE Syndics of the Cambridge University Press have undertaken the agency in the British Empire (except Canada) of this journal, the first number of which has recently appeared. The journal will be the official medium for the presentation of data and analyses dealing with subjects coming within its scope, and it will include the proceedings of the Association, reports of scientific research, and complete statements of official methods, the aim of the Association being to secure uniformity and accuracy in the methods, results, and modes of statement of the analysis of fertilisers, soils, feeding stuffs, and agricultural products of all kinds. The first number contains the minutes of the proceedings of the Thirtieth Annual Convention, held at Washington, D.C., in November, 1913, and the copious reports on various analytical methods and the recommendations of the members who subjected them to special tests are reproduced in full. The Association is doing valuable work in the United States, and British agricultural chemists and those interested in scientific agriculture will welcome the new journal.

First Aid in the Laboratory and Workshop. By ARTHUR A. ELDRIDGE, B.Sc., and H. VINCENT A. BRISCOE, D.Sc. London: Edward Arnold. 1915.

THIS useful little book contains short directions clearly expressing what is to be done in cases of emergency in the chemical laboratory or workshop. It is meant to be kept in the laboratory and consulted on the spot. The injuries of which it treats are those which are of comparatively frequent occurrence—burns, electric shock, poisoning, &c.—and the remedies prescribed are mostly simple and quickly applied, either before the doctor can be summoned or in cases when medical aid is unnecessary.

Investigaciones Experimentales sobre los Espectros de la Descarga Oscilante. ("Experimental Investigations of the Spectra of the Oscillating Discharge"). By ADOLFO T. WILLIAMS. Buenos Aires: Coni Hermanos. 1915.

THIS monograph contains descriptions of an experimental study of electrical influences (self-induction and capacity) upon the spectra of solutions of metallic salts. The metals investigated included calcium, barium, strontium, cadmium, magnesium, zinc, manganese, and copper, and after the experimental details have been given the results obtained are tabulated, and certain general conclusions are drawn. The hypothesis of Lockyer is also discussed and criticised, the author believing that some of his conclusions confirm and others contradict it.

OBITUARY.

SIR HENRY ROSCOE.

It is with regret we have to announce the sudden death, on Saturday last, the 18th inst., from heart failure, of the Right Hon. Sir Henry Enfield Roscoe, F.R.S., D.C.L., LL.D., Correspondent of the French Institute (Académie des Sciences). We reprint the following notice of his life and works from the *Times* of the 20th inst.:—

The loss to science is very great. A pupil and assistant of Bunsen at Heidelberg, Roscoe brought to Manchester, where he became a professor, a new spirit of research, which spread far and wide through the agency of his pupils and his chosen fellow-workers. With Schorlemmer he may be said to have created a school of chemistry. When later he entered Parliament as Liberal member for South Manchester he was often called upon by the Government as scientific adviser, and he also rendered great service as a member of Royal Commissions and Committees. But

he will be chiefly remembered for the work he did for the advancement of scientific research and for enlightening his fellow-countrymen as to the position which science ought to occupy in the national life.

Henry Enfield Roscoe was born in London on January 7, 1833. Of Unitarian stock, he was the son of Henry Roscoe, a barrister-at-law, and of Maria, daughter of Thomas Fletcher, of Liverpool, and grandson of William Roscoe, the author of the *Lives of Lorenzo di Medici* and *Leo X.*, and some time Whig member for Liverpool. He went to Liverpool High School, and learnt chemistry from Balmain, the inventor of luminous paint. Next, at University College, London, he worked under Thomas Graham and A. W. Williamson. But in the autumn of 1852, after taking his B.A. degree with the prize of £10 in chemistry, he went to the University of Heidelberg, and became, with Lothar Meyer, Quincke, and Dittmar, a pupil of Robert Wilhelm Bunsen. It was the making of him; he became the assistant and friend of his master, and the deep affection between them lasted through life. Bunsen set Roscoe to work on the solubility of chlorine in water when mixed with hydrogen in one of the monk's cells that formed the upper rooms of the laboratory, which had originally been a monastery. This piece of work developed into the splendid joint research on photochemical action published between 1855 and 1863, and Roscoe made later and independently a very large number of investigations of total daylight according to the methods devised by the two collaborators. When Williamson succeeded to Graham's chair at University College he invited Roscoe to be his official assistant in the Winter Session of 1855-6. Roscoe accepted, but returned to Heidelberg for some months in 1856, and in the autumn of that year began independent teaching as a lecturer in a military school at Eltham, and started a consulting practice with W. Dittmar.

In Manchester.

In 1857 he was appointed Professor of Chemistry in Owens College, Manchester, and for the next thirty years his fortunes and those of the college were closely bound together.

Owens College was then in a bad way. The landlord of the first house Roscoe wished to take in Manchester refused him as a tenant on the ground that the college would probably close its doors in a twelvemonth. But with Principal J. G. Greenwood, also newly appointed, Roscoe succeeded in turning the failure into a splendid success. Roscoe's system was that every student after pursuing a course of qualitative and quantitative analysis should be encouraged to undertake a research, under the guidance of Roscoe himself or some other member of the staff. "The spirit of research," he wrote, "must be in the air of the laboratory." It is largely due to him if in England this now sounds as a truism. It was in the laboratory rather than the lecture-room that he influenced his students. His singularly accurate knowledge of men was displayed in the choice of his fellow-workers, first William Dittmar and afterwards Carl Schorlemmer, who came to England in 1861, and eventually held the first chair of organic chemistry in this country. The names of Roscoe and Schorlemmer are inseparably united in the authorship of their great "Treatise on Chemistry," published 1877-88; the wide and deep erudition of Schorlemmer, and the gift possessed by Roscoe of appealing to the average intelligence made the book the only large modern treatise on chemistry in English which is readable. But the greatest work of the two men was the creation of a school of chemistry. Their pupils are many and famous. Roscoe cared no less for the advance of the college as a whole; he worked well with his distinguished colleagues, and the creation of the Victoria University was the result of their efforts, though in its original form it was not the University of Manchester for which they had long fought. Owens had been founded on the model of University College, London, but Roscoe and his friends saw that success

could only be achieved by creating the University as a great integral portion of the community in which it was placed, by adapting itself to local needs and by inspiring new civic ideals. Roscoe's many-sided work for the furtherance of this idea, at first almost unconscious and gradually becoming more and more explicit in its aims, was probably the most fruitful work of his life. He was also Vice-Chancellor of the University of London during the critical period of six years (1896-1902) which included the passing of the Act of 1898 and the transformation of the University from an examining body into a teaching body.

Political and Public Service.

In 1885 Roscoe was elected Liberal member for South Manchester, and he had to sever his long connection with the Owens College. The College Council placed on record their appreciation of his services and elected him Emeritus Professor, and he shortly after became a Governor. He frequently came to Manchester in after years. He was re-elected for South Manchester in 1886 and again in 1892, but in 1895 he was defeated as a Liberal Unionist, and his political work came to an end. He felt when he retired that "he had had enough." His services were often called upon by Government in scientific matters. In 1881 he was appointed member of the Royal Commission on Technical Education, which led to the passing of the Technical Instruction Acts of 1889 and 1890 and to the devotion of large sums of public money to the service of technical education. For his services on the Commission he was knighted in 1884.

Work as a Chemist.

In pure chemistry some of his most important published memoirs are those dealing with vanadium. He showed that the substance supposed by Berzelius to be metallic vanadium was in reality an oxide of that metal; he carried out an extensive research on the vanadium compounds, and showed the relationship of certain vanadates with the isomorphous phosphates and arsenates. Among his other researches may be mentioned those on the distillation of dilute acids and on perchloric acid. As a writer of elementary text-books of chemistry he had extraordinary success. His "Elementary Lessons," first published in 1866, were translated into many languages. His "Primer of Chemistry" had scarcely less success; it is, indeed, a little masterpiece. In 1895 he published a life of John Dalton for the "Century Science Series," of which he was editor, and in 1896, with Dr. Harden, "A New View of the Origin of Dalton's Atomic Theory," in which use was made of the Dalton manuscripts belonging to the Manchester Literary and Philosophical Society. A fourth edition of his "Lectures on Spectrum Analysis" was revised by Prof. Schuster in 1886. If Roscoe can hardly be placed in the first rank of chemists, his own researches were sufficient to lend authority to his views on scientific education, and no man in England of his generation except Huxley did as much for the progress of scientific education generally. He had true enthusiasm for his ideals, and his knowledge of the world helped to make that enthusiasm effective.

In person Roscoe was both tall and broad; his large face, somewhat boyish-looking till he was long past middle age, corresponded with his genial and kindly manner. To speak with him on his own subject was to discover his deep fund of modesty. He married in 1863 Lucy, daughter of Mr. Edmund Potter, F.R.S. (some-time member for Carlisle), and of Dinting, near Manchester. His only son died in early manhood; he is survived by his widow and by two daughters, of whom one is married to Mr. C. E. Mallet, formerly M.P. for Plymouth.

He received many official distinctions. He was elected F.R.S. in 1863, and was awarded a Royal Medal by the Royal Society for his photochemical researches and his work on vanadium in 1873.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxi. No. 17, October 26, 1915.

Preparation of Alkaline Nitrates from Calcium Nitrate.—H. Le Chatelier and B. Bogitch.—The preparation of ammonium nitrate from calcium nitrate is very simple from a chemical point of view, and the reaction should be practically complete in view of the slight solubility of calcium sulphate, $\text{Ca}(\text{NO}_3)_2 + (\text{NH}_4)_2\text{SO}_4 = \text{CaSO}_4 + 2\text{NH}_4\text{NO}_3$. However, the separation of the calcium sulphate precipitated is very difficult, and at the ordinary temperature a white paste is obtained which is almost impossible to filter. The authors first tried to increase the size of the crystals by allowing them to remain for a long time in contact with the solutions, either at the ordinary temperature or at 100° . The results were not satisfactory. However, they had observed that if very fine calcium sulphate is heated to 150° with water in a sealed tube large needles of the hemihydrate, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, are obtained, and by this means it was found possible to decant the liquid off the precipitate. The transformation begins at 120° , but the size of the crystals increases as the temperature is raised. The crystals consist of mixed crystals of the anhydrous sulphate and the hemihydrate. By working at a temperature of 150° and washing rapidly it is possible to obtain at once a nitrate of ammonium which is quite free from salts of calcium.

Bulletin de la Société Chimique de France.

Vol. xvii.-xviii., No. 15—16, 1915.

Dithio-trimercuric Salts.—G. Denigès.—When a mixture of mercuric sulphate and water is shaken with carbon disulphide, the following reaction occurs:— $3\text{HgSO}_4 + \text{CS}_2 + 2\text{H}_2\text{O} = \text{Hg}_3\text{S}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4 + \text{CO}_2$. If mercuric nitrate is used instead of the sulphate, a white crystalline thionitrate is obtained, and a thiocloride can be prepared similarly. Dithio-mercuric organic salts can be obtained by dissolving mercuric oxide in the organic acid and water, and treating with carbon disulphide. When subjected to the action of an alkali they give rise first to a hydrate and then to the oxide, $\text{Hg} \begin{smallmatrix} \text{S} - \text{Hg} \\ \text{S} - \text{Hg} \end{smallmatrix} \text{O}$. Dithiotrimercuric salts are also prepared by the action of COS or CSNH on precipitated mercuric salts. Owing to the characteristic crystalline form of the dithio-mercuric salts, their insolubility, and the relatively small amount of carbon disulphide necessary for their formation they can be used for the micro-chemical detection of this sulphide.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Chemical and Dye Works.—A correspondent is anxious to obtain a complete list of all chemical and dye works in the British Isles. We shall be glad if any of our readers can refer us to any publication giving this information.

MEETINGS FOR THE WEEK.

TUESDAY, Dec. 28th.	} Royal Institution, 3. (Christmas Lectures, adapted to a juvenile auditory). "Wireless Messages from the Stars," by Prof. H. H. Turner.
THURSDAY " 30th.	
SATURDAY, Jan. 1st	

THE CHEMICAL NEWS.

VOL. CXII., No. 2927.

NOTES ON FAT ANALYSIS.

I. SOLUBLE AND INSOLUBLE FATTY ACIDS.

By F. H. SMITH.

We have examined a number of samples of fats for the soluble acids, by the method of Morse and Burton ("Methods for Analysis of Butter," *Am. Chem. Journ.*, 1883, x., 322), and have combined into one procedure the determinations of saponification value, insoluble fatty acids, soluble fatty acids, and mean molecular weight of insoluble acids, by observing certain changes in the details of the method. All these determinations may be made in very nearly the same time required for the soluble acid determination alone, in the original method.

The most widely used method for determining the insoluble acids in fats is that proposed by Hehner and Angell ("Butter, Analysis and Adulteration," 1874). This author saponifies

variability in the action of carbon dioxide, even when precautions are used to subject the samples to the same treatment as far as possible. The higher results in B are due to presence of varying amounts of carbonic acid in the solution of soluble acids.

We give the method we have adopted and which has proven entirely satisfactory in this laboratory.

Five grms. of the oil or fat are weighed into a weighed Erlenmeyer (250 cc.) flask, and 50 cc. of approximately half-normal alcoholic potash (KOH) are added.

The flask is fitted to a reflux condenser, and heated on the water-bath until saponification is complete as evidenced by a clear solution free of fat globules. At the same time an exactly equal amount of the potash solution is measured into a similar flask, and heated under reflux condenser for the same length of time.

The fat completely saponified, the flask is removed and allowed to cool somewhat; then 15 to 20 drops of phenolphthalein solution are added, and the excess alkali titrated with half-normal HCl. The saponification value is calculated from these results. The flask containing the soap solution is placed in a water-bath and the alcohol evaporated. When nearly dry a little more water is added and again evaporated, thus removing the alcohol. The residue is dissolved in 100 cc. warm water. Such an amount of half-normal HCl is added as will make the total amount

SAMPLE 1.—Butter Fat.

	A.		B.	
Weight of sample	5.2000	5.0250	4.8125	4.4935
Cc. 0.5% N KOH used by sample .. .	42.58	41.14		
Saponification number .. .	229.68	229.64		
Cc. 0.1% N KOH to titrate soluble acids ..	29.50	28.50	28.20	27.00
Neutralisation number of soluble acids (a) ..	31.82	31.81	32.87	33.70
Calculated as per cent butyric acid .. .	4.99	4.99	5.15	5.28
Per cent insoluble acids .. .	89.01	88.87	88.81	88.83

SAMPLE 2.—Acetylated Fat.

	A.			B.			
Weight of sample .. .	2.2240	2.1140	2.2120	2.1950	2.2130	2.1305	2.2235
0.5% N KOH used .. .	18.67	17.69	18.56				
Saponification value .. .	235.47	234.72	235.35				
0.1% N KOH to titrate soluble acids .. .	14.68	13.96	14.54	15.95	14.90	17.14	17.88
Neutralisation number of soluble acids (a) ..	37.03	37.00	36.87	40.76	37.77	45.13	45.11

(a) Neutralisation number denotes milligrams. of KOH used to titrate soluble acids from each grm. of fat.

the fat, evaporates the alcohol, dissolves the soap in water, frees the fatty acids with mineral acid, and collects and weighs the insoluble acids. An attempt was made to collect the soluble acids from this procedure, but the determinations were generally unsatisfactory on account of the action of atmospheric carbon dioxide on the free alkali during evaporation of the alcohol. This is shown by the data recorded in the table.

In nearly every case, when the free alkali was titrated with mineral acid before evaporating the alcohol, closely agreeing results were obtained with the checks. This is due to the removal of the free alkali from action of the air. Soaps are affected very little by carbon dioxide in the air, and the soap solution may be evaporated with little danger of error from this agency being introduced.

In the table are given the results from a sample of butter fat. The first figures are from the pure fat, and the second series gives the results obtained after the fat was acetylated, and were made to determine the acetyl value. Samples A were treated according to the procedure given below, the free alkali being titrated before evaporating to dryness. In case of B samples the alcohol was evaporated, the soap dissolved in water, and acids liberated by adding mineral acid. The results indicate the liability of loss of free alkali unless it is titrated immediately after saponification. The results obtained with Sample 2 show the

added to the sample exceed by 1.00 cc. the amount used by the blank. The flask is then loosely stoppered and heated on the water-bath until the fatty acids rise to the top in a clear layer.

The flask is cooled in ice-water until the acids are solidified, after which the liquid portion is decanted through a filter into a litre measuring flask, keeping the disc of fatty acids in the Erlenmeyer. A little cold water is added, and the insoluble acids rinsed off, the water being added to that in the measuring flask. 150 to 200 cc. hot water is added to the Erlenmeyer, and it is then placed on the bath until the acids are melted. The contents are thoroughly mixed by a rotary movement of the flask, taking care that contents do not touch the stopper in neck of flask. The flask is placed in ice-water as before, the acids allowed to solidify, and the water poured through the filter into the measuring flask. The melting, shaking, cooling, and decanting process is repeated three times, all the wash-water being received in the measuring flask. The insoluble acids are kept in the original Erlenmeyer. The measuring flask is filled to the mark, and two 100 cc. portions titrated with tenth-normal KOH. The readings are multiplied by 10 and 5.00 subtracted from the result; this corresponds to the 1.00 cc. excess acid added to facilitate separation of fatty acids. The results may be recorded as mgrms. KOH required to neutralise the soluble acids

from 1 gm. of fat, or may be calculated as butyric acid.

The filter is allowed to dry, the Erlenmeyer containing the insoluble acids is placed beneath the funnel, and the particles of insoluble acids on the filter rinsed through the funnel into the flask with a small stream of absolute alcohol from wash-bottle. When the acids are thoroughly dissolved from the funnel the flask is placed on the water-bath, and the alcohol evaporated and the acids dried. Drying for too long may result in loss of acids or in oxidation changes, the former lowering the results and the latter raising them. Two hours drying is usually sufficient. After cooling the flask is weighed, then heated at 100°, and weighed again. This is continued until the weight is nearly constant.

The insoluble acids may then be dissolved in alcohol, and titrated with half-normal alkali to determine the neutralisation number or mean molecular weight. The Erlenmeyer flask always loses a few mgrs. in weight during the saponification process, but the loss is generally inappreciable and may be neglected.

Determination of saponification number, soluble fatty acids, insoluble fatty acids, and mean molecular weight have been made in one series of operations and from the same sample.

The free alkali should in every case be titrated before the alcohol is evaporated, otherwise error in the determination through absorption of carbon dioxide from the air may result.

The method as given has proven entirely satisfactory, in case of the large number of samples examined in this laboratory.

Chemical Laboratory, Georgia Experiment Station,
Experiment, Ga.

THE THERMAL DECOMPOSITION OF HYDROGEN PEROXIDE IN AQUEOUS SOLUTION.*

(PRELIMINARY NOTE).

By WILLIAM CLAYTON.

(Concluded from p. 310).

To return to the problem of the decomposition of H_2O_2 in alkaline solutions, it may be mentioned that the caustic soda employed had been precipitated by alcohol. It was used at various concentrations, but satisfactory results could not be obtained. A single illustration will serve to indicate the degree of variability observed.

1.5 per cent H_2O_2 in N, 10 NaOH.
(Duplicate Experiments).

Experiment I.			Experiment II.		
t.	x.	K (mono-molecular).	t.	x.	K.
24	12.45	0.011016	26	16.10	0.01142
35	15.40	0.010306	53	21.50	0.00887
46	16.85	0.009067	109	25.80	0.00629
64	18.90	0.007998	241	29.50	0.00429
157	19.73	0.004670	313	30.53	0.00390
201	21.00	0.004044	∞	32.50	
257	22.15	0.003503			
∞	[27.30]				

It will be observed that K falls as the reaction proceeds.

Similar variations in results were obtained in many other cases, e.g., using NaCl, mixtures of NaCl and NaOH, Na_2SO_4 , and $NaNO_3$. A search of the literature showed that previous workers had met with similar difficulties, e.g., Tammann who investigated the effect of alkali upon the peroxide (*Zeit. Phys. Chem.*, 1889, iv., 440). Tammann attributes the variability to the presence of iron oxide in the alkali. This conclusion appears to be

probable inasmuch as the stock solution employed for the present experiments deposited on long standing a light brown precipitate of iron hydroxide. To test this point directly a solution of H_2O_2 (1.5 per cent) in good conductivity water had a trace of colloidal iron hydroxide added to it, and the rate of decomposition at 50° C. was followed. The mean velocity constant was 0.00077, whilst that with conductivity water alone is of the order 0.00010. That is, the velocity constant in presence of the iron is seven times that in its absence.

The question of the influence of the surface of the containing vessel has already been referred to. Lemoine showed that a solution of H_2O_2 at 21° C., normally requiring fifteen days for half-decomposition, required only three minutes when placed in a silvered tube. The writer has confirmed this result, viz., a reaction (1.5 per cent H_2O_2 at 60° C.) normally requiring twenty three hours for half-decomposition went to completion in less than half-an-hour when kept in a silver bottle. In this connection, Spring had already shown (*Bull. Acad. Roy. Belg.*, 1895, [3], xxx., 32) that a solution of H_2O_2 would keep well in a vessel of clean smooth platinum, but the slightest scratch accelerated the reaction markedly. Further, it is generally accepted that quartz flasks are more advantageous than glass ones for conserving H_2O_2 , and, following Brühl's observation that a waxed surface is very inert, wax-lined bottles are used commercially for storing the peroxide.

The results obtained by the writer, however, seem to show that at temperatures from 50° C. upwards the nature of the containing vessel (provided it is not metallic) is not so vital as the degree of "purity" of the water which is employed as the solvent. With very "pure" water, the results show that the rate of decomposition is approximately the same whether the flask be of glass, quartz, or wax.

Rate of Decomposition of H_2O_2 in Water of Various Degrees of "Purity."

Previous workers do not appear to have laid particular stress upon the "purity" of the water. It was considered, in the light of the foregoing work on the influence of colloids, that perhaps even good conductivity water was in reality unsuitable. Accordingly, a series of experiments was carried out in four different flasks, viz., (1) Jena glass, (2) quartz flask X, (3) quartz glass Y, (4) wax-lined flask. A number of solutions containing 1.5 per cent H_2O_2 were made up in the following "solvents":—

- Tap water.
- Ordinary distilled water (from block-tin condenser).
- Conductivity water (conductivity 1.1 gemmho).
- "Pure water I."
- "Pure water II."

"Pure water I." was prepared as follows:—A silver-plated copper boiler (3 pints capacity) was filled with freshly distilled water, which was then re-distilled, the steam passing through two quartz spirals, the first to serve as a spray trap, the second as a condenser. The water was collected directly in the reaction flask. (No glass was employed in the apparatus).

TABLE I.

Tap Water as Solvent. 1.5 per cent H_2O_2 at 60° C.

$K = \frac{1}{t} \log \frac{a}{a-x}$, $t_{\frac{1}{2}}$ = time of half decomposition.

Quartz Flask X.

Experiment a.			Experiment b.		
(mins.).	x.	K.	(mins.).	x.	K.
21	1.15	0.00115	21	1.15	0.00115
128	6.65	128	128	6.65	128
255	12.45	151	255	12.45	151
292	13.85	158	292	13.85	158
343	15.35	163	343	15.35	163
474	18.45	188	474	18.45	188
	[21.15]			[21.15]	

$t_{\frac{1}{2}} = 3$ hrs. 33 mins.

$t_{\frac{1}{2}} = 4$ hrs. 26 mins.

* A Paper read before the Faraday Society, October 19, 1915.

TABLE II.

Distilled Water as Solvent. 1.5 per cent H_2O_2 at $60^\circ C$.

Quartz Flask V.

Experiment a.			Experiment b.		
t.	α.	K.	t.	α.	K.
60	0.50	0.000166	81	1.15	0.000291
195	1.20	124	239	2.30	207
416	3.40	175	418	3.95	208
1389	8.85	160	1413	9.75	182
1509	9.40	160	1839	11.50	177
2791	13.70	151		21.75	
3184	14.80	152			
4269	16.95	149			
	22.00				

$t_1 = 32$ hrs. 34 min.

$t_1 = 28$ hrs.

TABLE III.

Conductivity Water as Solvent. 1.5 per cent H_2O_2 at $60^\circ C$.
Repetition of same experiment in same flasks under identical conditions.

Conductivity water employed (1.1×10^{-6} mho.).

(1) Jena Glass.

t.	α.	K.
99	0.55	0.000122
214	1.50	157
420	3.00	167
1394	9.30	193
1523	9.95	194
1752	11.56	212
2844	18.10	352
3000	18.40	357

$t_1 = 25$ hrs. 12 mins.

(2) Quartz X.

t.	α.	K.
99	1.20	0.000260
216	2.45	251
410	4.30	245
1399	11.40	246
1528	12.05	246
1730	13.00	246
2848	16.70	247
2985	17.00	246

$t_1 = 20$ hrs. 12 min.

47	0.65	0.000293
178	2.20	266
318	3.70	267
1316	10.60	235
1492	11.20	225
1683	12.53	238

$t_1 = 20$ hrs. 12 min.

108	1.15	0.000225
261	3.55	306
1251	11.40	269
1438	12.50	271
1616	13.27	266

$t_1 = 18$ hrs. 36 min.

48	0.35	0.000153
129	0.55	0.00009
1106	7.80	0.000186
1346	8.85	180
2569	13.65	182
2923	14.60	182
4003	16.95	186

$t_1 = 27$ hrs.

48	0.65	0.000283
117	2.40	254
1105	8.45	201
1354	10.30	214
1482	11.30	224
2574	16.50	256
2924	17.40	258
4008	20.15	337

$t_1 = 23$ hrs.

(3) Quartz V.

45	0.30	0.000138
1098	5.35	116
1355	7.20	130
1488	7.85	136
2580	11.60	135
2925	12.20	129
4004	15.05	136

$t_1 = 43$ hrs.

(4) Wax lined Flask

58	0.75	0.000270
276	8.35	272
383	4.55	275
1433	10.55	210
1758	11.70	200
2852	14.60	180

$t_1 = 23$ hrs. 50 mins.

92	0.75	0.000175
210	2.40	256
406	4.40	257
1390	9.80	201
1722	10.90	189
2839	14.30	181
2975	14.50	177

$t_1 = 28$ hrs.

TABLE IV.

"Pure Water I." as Solvent. 1.5 per cent H_2O_2 at $60^\circ C$.

Jena Glass.

t.	α.	K.
19	0.35	0.000144
161	0.50	0.000063
346	0.80	47
1377	1.95	29
2896	4.00	30
4248	5.40	29
5777	6.10	25
7068	7.82	27
8514	9.34	28
9963	10.96	30
	21.70	

$t_1 = 165$ hrs.

Quartz X.

Experiment a.			Experiment b.		
t.	α.	K.	t.	α.	K.
121	0.45	0.000077	137	0.85	0.000127
296	1.35	0.000094	321	1.55	0.000097
1048	4.60	0.000102	1301	2.47	40
1368	5.90	0.000105	2710	6.16	53
2480	9.85	111	4152	9.21	58
2958	11.10	110	5602	11.59	59
3981	13.30	109		21.56	
5475	16.05	115			
	20.95				

$t_1 = 45$ hrs.

$t_1 = 81$ hrs.

Quartz V.

Experiment a.			Experiment b.		
t.	α.	K.	t.	α.	K.
117	0.05	0.000009	144	0.80	0.000115
254	0.25	0.000021	297	1.30	0.000092
1365	2.55	43	1313	3.07	51
1844	3.30	42	2714	6.98	63
2867	5.40	46	4154	10.17	67
4362	8.05	50	5600	12.85	71
5870	10.20	51		21.30	
7198	11.75	51			
	20.35				

$t_1 = 98$ hrs.

$t_1 = 70$ hrs.

Wax-lined Flask.

Experiment a.

t.	α.	K.
53	0.15	0.000058
293	0.65	45
1295	3.85	65
1775	5.35	69
2796	7.55	66
3229	8.35	65
4275	10.30	65
5792	12.20	62
7135	13.55	59
	21.65	

$t_1 = 71$ hrs.

"Pure water II." was prepared as described above, with the addition that the quartz arm connecting the two spirals was heated to redness so that the dry steam might deposit any suspended matter.

The results obtained with these various solvents are appended in Tables I. to V.

It will be observed that with this solvent the lowest values so far have been obtained, viz., with quartz flask X and the wax-lined flask, the order of magnitude of K being 0.00002. This is approximately one-tenth of the value obtained with conductivity water, and, further, the rate in conductivity water is scarcely distinguishable from that in ordinary distilled water. It may be inferred, therefore, that the hydrogen and hydroxyl ions of the solvent do no

exercise an appreciable influence, but that the freedom of the solvent from colloidal organic matter is the factor of greatest importance.

At this stage the work had to be interrupted. Although the results are preliminary only, it is believed that the following conclusions are justifiable.

TABLE V.

"Pure Water II." as Solvent. 1.5 per cent H_2O_2 at 60° C.

Jena Glass Flask.			Wax lined Flask.		
t.	v.	K.	t.	v.	K.
165	0.30	0.0000375	234	0.10	0.000009
1198	2.10	381	1334	1.45	0.000026
2610	3.80	331	2637	2.70	25
4419	5.40	290	4124	4.10	26
6497	8.20	330	5559	5.00	24
7992	9.70	336	6946	5.85	23
9723	11.70	318	8485	6.90	23

[21 00]

$$t_{\frac{1}{2}} = 1.43 \text{ hrs.}$$

Quartz X.			Quartz Y.		
t.	v.	K.	t.	v.	K.
351	0.75	0.0000490	220	0.45	0.000048
1440	1.70	282	1337	2.15	40
2730	2.55	238	2608	4.45	45
4202	3.05	180	4000	7.55	56
5660	4.30	196	5440	10.20	63
7056	5.05	190	6856	12.55	74
8589	6.05	193	7374	14.50	89

Summary.

1. The rate of thermal decomposition of aqueous solutions of hydrogen peroxide is extremely sensitive towards extraneous organic matter in the colloidal state. Mechanical factors, such as volatility and the presence or absence of stirring, do not exercise an appreciable influence.

2. The chief factor in the decomposition has been shown to be the degree of purity of the water. Thus in tap water the rate of decomposition is fully fifty times that in the purest specimen of water we have yet prepared.

3. In the light of these results previous work upon the thermal decomposition of H_2O_2 , especially the comprehensive research of Lemoine, must be considered as of doubtful value, as no special precautions appear to have been taken in regard to the solvent.

4. In view of the marked effect produced by the solvent it remains an open question as to whether the surface of the vessel exerts an appreciable effect or not; it is possible that effects previously attributed to the surface may have been due to slight variations in the organic matter content of the solvent.

In conclusion, the author wishes to express his thanks to Prof. W. C. McC. Lewis for suggesting and supervising the research.

INTRODUCTION TO THE THEORY OF RELATIVITY.*

(SUPPLEMENTARY NOTE).

By F. H. LORING.

AN opportunity was missed in not referring before to the great work of Prof. Zeeman, recently published, which is a remarkable confirmation of the Lorentz extension of the expression of Fresnel for the coefficient of drag in the experiment of Fizeau, since the result of this new experimental work is apparently in full accord with the Relativity Theory. I will not take up further space here, but the reader who is interested in these important matters should consult the following sources of information:—

Silberstein's "Theory of Relativity," p. 55.

Cunningham's "Principle of Relativity," p. 62, Section II.

* See CHEMICAL NEWS, cxii., 226, 236, 248, 260, 306.

Science Abstracts, Section A, 1915, pp. 281 and 597.

Nature, December 16, 1915, p. 430.

Cunningham's "Relativity and the Electron Theory" 1915 (just published by Longmans, Green, and Co., this being one of the Monographs-on-Physics Series, edited by Sir J. J. Thomson and Dr. Frank Horton), pp. 40-43. Cunningham, by the way, points out that the experimental value 0.434, given by Michelson and Morley, "appears to be an arithmetical error, the data given leading to 0.442."

I may add, that the calculated value from Fresnel's formula would be 0.438 for sodium light, say of wave-length 5893 (mean). Taking a wave-length of 5461 Prof. Zeeman now gets the experimental value (0.454) in agreement with the one calculated from the Lorentz extension formula, which allows for dispersion, namely, 0.451, whereas by the Fresnel formula the corresponding value would be 0.439. For different wave-lengths (colours) a remarkably close range of "Lorentz coefficients" were obtained by Prof. Zeeman, the dispersive effect being confirmed.

MOTOR-CAR STEEL.

By SERGIUS KERN, M.E., Petrograd.

AT present there is such a vast number of classes of steel recommended and used in motor-car manufacture, that often it is difficult to choose the metal for forging motor-car parts.

I used with success for this purpose a crucible steel which was not doctored by any addition of expensive metals or alloys, so greatly recommended, but was prepared from very clean raw materials in a coke crucible furnace holding four crucibles.

Raw Materials Used.

1. Puddled iron, containing about 0.1 per cent of carbon, 0.03 per cent of phosphorus, 0.02 per cent of sulphur.

2. Roundings from rivet holes in soft open-hearth steel ship-plates, containing 0.16 per cent of carbon, 0.04 per cent of phosphorus, 0.03 per cent of sulphur, and 75 per cent of manganese.

3. Nickel in cubes, containing 98.5 per cent of metal.

The charge of each crucible consists of—

	Russian pounds.
Puddled iron	40
Roundings	60
Nickel	1

Total 101

Additions.

Put into the crucible with the charge—

Ferro-manganese (80 per cent) 0.10

Put into crucible before taking it out—

Silico-spiegel (containing 12 per cent of silicon and 18 per cent of manganese) 1.00

Ferro-silicon (containing 50 per cent of silicon) 0.15

Ferro-manganese (80 per cent) 0.10

This steel contains—

Carbon	0.45 per cent
Manganese	0.48 "
Silicon	0.30 "

It may be cast into moulds and into ingots; the latter for forging purposes.

On an average the steel castings give about 45 tons per square inch tensile strength and 10 per cent elongation n 2 inches. Forgings give 48 tons tensile strength and 18 per cent of elongation.

THE CONDUCTIVITY AND VISCOSITY OF
SOLUTIONS OF ELECTROLYTES IN
FORMAMID.*

By P. B. DAVIS, W. S. PUTNAM, and HARRY C. JONES.

(Concluded from p. 308).

Sodium Chromate.

TABLE V. gives the results for sodium chromate. They are of the usual order of magnitude, except for the N/1600 solution. At each temperature the increase in conductivity between the N 800 and N/1600 solutions is 59 per cent, which is probably due to chemical action or decomposition, instead of to an increase in ionisation. Formic acid is a strong reducing agent. Formamid may be considered a formic acid in which a hydroxyl has been replaced by an amido group. Both the hydroxyl and amino group are basic; therefore we might expect from this relationship that formamid would be a reducing agent. The reducing action of formamid will also be discussed with the results for mercuric chloride. Sodium chromate is a strong oxidising agent; hence it is not surprising that there should be chemical action between these two compounds when the chromate is in a highly ionised condition, as in a dilute solution. The percentage dissociations have not been calculated, because the conditions just referred to introduce an uncertainty regarding them.

Mercuric Chloride.

The conductivity of aqueous solutions of mercuric chloride is too small to be measured, but in formamid, on account of its greater dissociating power, the conductivity is measurable, and increases as dilution increases in the usual way up to the N₄₀₀ solution. The conductivity values for the N/1000, N/1600, and N/3200 solutions clearly result from some decomposition, probably of the solvent. The conductivity of barium chloride at complete dissociation is 55.86 at 25°. The large value, 134.49, for the N₁₀₀₀ mercuric chloride solution shows that it is not due to dissociation. Assuming that at complete dissociation the conductivity of mercuric chloride would be of the same order of magnitude as of barium chloride, the dissociation of the N₄₀₀ solution would be about 1.0 per cent, increasing to about 7.0 per cent for the N₄₀₀ solution. Silver chloride is precipitated in the N₄₀₀ solution by silver nitrate. By standing in the sunlight for a short time a heavy precipitate of metallic silver is formed, showing again the reducing action of formamid.

To recover the solvent from the mercuric chloride by vacuum distillation required several more distillations than usual. Metallic mercury was found in the receiver after the first distillation, showing again the reducing action of formamid. It is possible that the liberated chlorine formed a salt with the formamid which was easily dissociated, since the conductivity of the first fraction of the distillate was very high, and was lowered only a small amount by successive distillations. Repeated distillation, however, gave the solvent used for the solutions of the caesium salts.

Cobalt Bromide.

The green anhydrous cobalt bromide gives a pink solution in formamid as in water. After the determinations were made a mixture of solutions was distilled to recover the formamid. The mixture contained mercuric chloride and cobalt bromide. As already stated the mercuric chloride was reduced to metallic mercury. The dry residue in the distillation flask had the brilliant blue colour of anhydrous cobalt chloride, showing that the free chlorine from the mercuric chloride had replaced the bromine in the cobalt bromide.

TABLE XVI.—Rubidium Nitrate in Formamid.

Molecular Conductivity and Dissociation.

V.	Molecular conductivity.			Dissociation.		
	15°	25°	35°	15°	25°	35°
4	16.20	20.79	25.85	77.7	77.6	77.6
10	18.85	24.07	30.00	90.1	89.8	90.1
50	20.22	25.97	32.23	97.0	96.9	96.8
100	20.85	26.80	33.31	100.0	100.0	100.0
200	20.76	26.68	33.02			
K	2.17×10^{-5}			3.17×10^{-5}		

Viscosity and Fluidity.

V.	η 15°	η 25°	η 35°	ϕ 15°	ϕ 25°	ϕ 35°
4	0.04586	0.03430	0.02673	21.81	29.16	37.41
10	0.04417	0.03346	0.02622	22.64	29.89	38.15
Solv.	0.04284	0.03256	0.02561	23.34	30.71	39.05

TABLE XVII.—Caesium Chloride in Formamid.

Molecular Conductivity and Dissociation.

V.	Molecular conductivity.			Dissociation.		
	15°	25°	35°	15°	25°	35°
4	16.83	21.69	27.15	78.6	78.8	78.7
10	18.75	24.09	30.03	87.6	87.5	87.1
200	21.40	27.54	34.49	100.0	100.0	100.0
400	21.06	27.15	34.11			
K	1.34×10^{-5}			1.72×10^{-5}		

Viscosity and Fluidity.

V.	η 15°	η 25°	η 35°	ϕ 15°	ϕ 25°	ϕ 35°
4	0.04735	0.03578	0.02789	21.12	27.95	35.86
10	0.04481	0.03395	0.02654	22.32	29.46	37.68
Solv.	0.04317	0.03245	—	23.16	30.18	—

TABLE XVIII.—Caesium Nitrate in Formamid.

Molecular Conductivity and Dissociation.

V.	Molecular conductivity.			Dissociation.		
	15°	25°	35°	15°	25°	35°
4	17.00	21.79	27.10	78.2	78.1	78.3
10	18.90	24.23	29.92	86.9	86.8	86.4
100	21.36	27.42	33.99	98.2	98.3	98.2
200	21.75	27.90	34.61	100.0	100.0	100.0
400	21.59	27.64	34.43			
K	1.34×10^{-5}			1.72×10^{-5}		

Viscosity and Fluidity.

V.	η 15°	η 25°	η 35°	ϕ 15°	ϕ 25°	ϕ 35°
4	0.04614	0.03478	0.02725	21.67	28.75	36.70
10	0.04456	0.03362	0.02632	22.44	29.74	37.90
Solv.	0.04317	0.03245	—	23.16	30.81	—

TABLE XIX.—Lithium Nitrate in Formamid.

Molecular Conductivity and Dissociation.

V.	Molecular conductivity.			Dissociation.		
	15°	25°	35°	15°	25°	35°
2	12.16	15.57	—	66.0	65.8	—
4	14.10	18.07	—	76.5	76.4	—
10	16.11	20.58	25.54	87.5	87.0	86.9
50	17.38	22.29	27.68	94.4	94.2	94.1
200	18.42	23.66	29.34	100.0	100.0	99.8
400	18.23	23.63	29.40	—	—	100.0
K						

Viscosity and Fluidity.

V.	η 15°	η 25°	η 35°	ϕ 15°	ϕ 25°	ϕ 35°
2	0.05191	0.03873	0.03019	19.26	25.82	33.12
4	0.04720	0.03571	0.02786	21.19	28.00	35.89
10	0.04460	0.03157	0.02646	22.42	31.68	37.79
Solv.	0.04272	0.03196	0.02503	23.41	31.29	39.95

* From the *Journal of the Franklin Institute*, November, 1915.

TABLE XX.—Barium Chloride in Formamid.

V.	Molecular conductivity			Dissociation.		
	15°	25°	35°	15°	25°	35°
10	30.58	40.00	50.12	70.3	71.6	70.1
50	38.06	49.43	61.90	87.5	88.5	86.6
200	40.38	52.48	65.93	92.9	93.9	92.2
800	43.45	55.82	70.38	99.9	99.9	98.5
1600	43.48	55.86	71.48	100.0	100.0	100.0
K	1.58 × 10 ⁻⁵	2.02 × 10 ⁻⁵	2.45 × 10 ⁻⁵			

Viscosity and Fluidity.

V.	η 15°	η 25°	η 35°	ϕ 15°	ϕ 25°	ϕ 35°
10	0.04941	0.03702	0.02878	20.24	27.01	34.75
Solv.	0.04301	0.03221	0.02510	23.25	31.05	39.84

TABLE XXI.—Mercuric Chloride in Formamid.

Molecular Conductivity.

V.	Molecular conductivity.		
	15°	25°	35°
4	0.43	0.59	0.83
10	0.63	0.87	1.27
50	1.09	1.56	2.22
200	1.74	2.53	3.68
400	2.73	4.15	5.82
1000	—	134.49	—
1600	—	101.13	—
3200	—	75.35	—
K	1.30 × 10 ⁻⁵	1.65 × 10 ⁻⁵	2.03 × 10 ⁻⁵

Viscosity and Fluidity.

V.	η 15°	η 25°	ϕ 15°	ϕ 25°
4	0.04688	0.03527	21.33	28.35
10	0.04496	0.03376	22.25	29.62
Solv.	0.04301	0.03221	23.25	31.05

TABLE XXII.—Cobalt Bromide in Formamid.

Molecular Conductivity and Dissociation.

V.	Molecular conductivity.			Dissociation.		
	15°	25°	35°	15°	25°	35°
10	27.11	35.35	44.30	60.9	61.4	60.7
50	34.70	45.01	56.56	78.0	78.1	77.5
200	39.00	50.34	—	87.7	87.4	—
800	44.48	57.60	72.95	100.0	100.0	100.0
1600	41.83	53.96	68.70			

Viscosity and Fluidity.

V.	η 15°	η 25°	η 35°	ϕ 15°	ϕ 25°	ϕ 35°
10	0.04892	0.03699	0.02867	20.44	27.03	34.88
Solv.	0.04301	0.03221	0.02510	23.25	31.05	39.84

Cæsium Nitrate and Chloride.

For several years past this laboratory has been unable to obtain any cæsium salts for its investigations in conductivity and viscosity. Recently, some cæsium sulphate was obtained through the co-operation and courtesy of Prof. James Lewis Howe, of Washington and Lee University. The sulphate was converted into the nitrate and chloride, and the conductivity and viscosity of their solutions were determined. The results are recorded in Tables XVII. and XVIII.

A survey of the work on the salts of all the alkali metals shows that conductivity values for the cæsium, rubidium, and potassium salts used are approximately the same, and for sodium and lithium are less. The same relation is true of the results obtained in aqueous solutions. Dissociation percentage is of the same order of magnitude for all the salts named. The conductivity results in connection with the dissociation percentage harmonise with the ionic

velocities. For cæsium, rubidium, and potassium the relative ionic velocities are 73.6, 73.5, and 70.6, respectively, and for sodium and lithium they are 49.2 and 39.8.

The most striking difference between these metals is shown by the atomic volume curve of Lothar Meyer (*Lieb. Ann. Suppl.*, 1870, vii., 354). This function increases by nearly regular steps from 12 for lithium to 72 for cæsium. In accordance with the theory of Jones and Veazey (*Publication No. 80*, 1907, Carnegie Institute of Washington; *Am. Chem. Journ.*, 1907, xxxvii., 405), to which reference has already been made, the percentage increases in the viscosity of the concentrated solutions over the viscosity of the solvent should be the smallest for cæsium salts, and should increase in the following order:—Cæsium, rubidium, potassium, sodium, and lithium. This relation comes out clearly by comparing the viscosity data for cæsium and rubidium salts (Tables XIII. to XVIII.) with those for sodium and lithium. The salts of rubidium and cæsium increase the viscosity of formamid much less than sodium and lithium salts (Tables III., IV., and XIX.). The difference in percentage increase is not as marked as the difference in the atomic volumes of the metal ions. The effect is partially suppressed by other factors. Consider the solution of a binary salt which is 80 per cent dissociated. Every hundred molecules of the salt gives, in solution, 80 ions, 80 cations, and 20 molecules. The 80 cations are only 44.5 per cent of the number of particles in the solution. It is only this 44.5 per cent of cations which have the atomic volume relations referred to above. The molecular volumes do not show this relation, and the atomic volumes of the anions are unknown.

Summary of Results.

The first five of the conclusions drawn below have been developed or confirmed by the investigations in this laboratory with other pure solvents, and have been shown by this investigation to hold true for formamid.

1. The greater the dielectric constant of a solvent the greater its dissociating power.
2. The greater the association factor of a solvent the greater its dissociating power.
3. The formation of solvates with formamid is indicated by those salts that form hydrates.
4. Solvated salts show larger percentage temperature coefficients of conductivity than non-solvated salts.
5. The order of magnitude of percentage temperature coefficients of conductivity is approximately proportional to the viscosity of the solutions.
6. Formamid is the first of the pure solvents studied with reference to the viscosity of solutions, in which none of the salts used produce negative viscosities. A satisfactory explanation of the above fact is apparent, if the very large association factor of the solvent is considered in connection with the theory of Jones and Veazey.
7. In regard to conductivity, dissociation, and effect on viscosity of solvent, cæsium salts are very closely allied to rubidium salts.
8. Mercuric chloride is more dissociated in formamid than in water.

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Homologues of Menthol.—Eyvind Boedtker.—The alkyl menthols can very readily be obtained by the action of sodium upon a solution of the corresponding alkyl menthone. The author has prepared some of these compounds and investigated their properties. He finds that both the densities and the refractive indices increase in the case of homologous acetates. As for the rotatory powers, it is a known fact that even from a lævo-menthone derivatives of opposite rotation are obtained. Benzyl menthol can be obtained by the reduction of benzylidene menthone.—*Bull. Soc. Chim. de France*, No. 15—16, 1915.

A NOTE ON THE
QUALITATIVE DETECTION AND SEPARATION
OF PLATINUM, ARSENIC, GOLD, SELENIUM,
TELLURIUM, AND MOLYBDENUM.

By PHILIP E. BROWNING.

PROBABLY the best working scheme for the qualitative separation and detection of platinum, gold, arsenic, selenium, tellurium, and molybdenum is that of Noyes and Bray (*Journ. Am. Chem. Soc.*, xxix., 137). Briefly stated the method is as follows:—The platinum is first separated as potassium chloroplatinate by evaporation with a potassium salt, and the arsenic in the filtrate is removed as ammonium magnesian arsenate by precipitation with magnesian chloride mixture in ammoniacal solution. The filtrate is then made acid with oxalic acid and warmed to precipitate the gold. The filtrate from the gold separation is evaporated almost to dryness and treated with strong hydrochloric acid and sodium sulphite, which removes the selenium, and on dilution of the filtrate and treatment with potassium iodide and sodium sulphite the tellurium is thrown down. After the removal of the tellurium and the addition of zinc and potassium sulphocyanide to the filtrate the red molybdenum sulphocyanide is obtained.

Recent work by a class of about forty in the application of this method to the analysis of a common solution showed a marked variation in results. With a considerable proportion of the class the tests for gold and arsenic were unsatisfactory and in some cases the tests for selenium and tellurium were doubtful. An investigation of the causes of these results revealed the following facts. First, that a solution of tellurous chloride when treated with a sufficient amount of ammonia to form the soluble ammonium tellurite and then with magnesian chloride mixture will give a floccy precipitate of magnesium and ammonium tellurite not easily soluble in an excess of ammonia. This reaction has been noticed by Heberlein and use has been made of it by him in the purification of crude tellurium (*Inaug. Dissert. Basel*, 1898, xxxvii.; "Gmelin-Kraut," 7th ed., iii. (2), 859). Second, selenious acid when treated with ammonia and magnesian chloride mixture tends to give, especially on warming, a crystalline precipitate of magnesium and ammonium selenite also quite insoluble under the conditions. Both this compound and that of tellurium have been described by Hilger (*Zeit. Anal. Chem.*, xiii., 132). Third, a solution of gold chloride when treated with ammonia gives a precipitate of fulminating gold; and after filtering and washing, gold may be detected both in the filtrate and in the precipitate.

From these facts it would seem probable that in the attempt to precipitate the arsenic acid as the ammonium magnesian arsenate one might under certain conditions not always easy to avoid, precipitate some of the compounds of gold, tellurium, and selenium, and not only vitiate the test for arsenic but also partly destroy the delicacy of the tests for gold, selenium, and tellurium.

To avoid these difficulties, one may leave the treatment with magnesian chloride mixture until after the gold, selenium, and tellurium have been removed and detected. On evaporating with bromine or nitric acid, the filtrate from the tellurium, which contains hydrochloric, sulphurous, and hydriodic acids, oxidation of the arsenic and molybdenum readily takes place, and the precipitation of the arsenic by magnesian mixture can be satisfactorily made. The molybdenum sulphocyanide is easily obtained in the filtrate by acidifying with hydrochloric acid and adding zinc and a sulphocyanide.

As a substitute for oxalic acid, hydrogen dioxide in alkaline solution has been found very satisfactory for the precipitation of gold.

In conclusion, it may be stated that the above indicated modification of the original method gave much more satisfactory results in the hands of the class.—*American Journal of Science*, xl., Oct., 1915.

NORTHAMPTON POLYTECHNIC INSTITUTE.

Prize Distribution, December 18, 1915.

ABSTRACT OF THE PRINCIPAL'S REPORT.

THIS, the eighteenth occasion on which the students and members have met together in order that the former may receive some of the rewards of their labours, finds us under the shadow of the great war, but fully determined to keep the record unbroken, and to publish to the world our belief in the solidity of the traditions which have now become part of the Northampton Polytechnic Institute.

The customary report which the Principal presents refers, as usual, more particularly to the work of the preceding session (1914-15), but in these stirring times may be permitted a greater latitude than usual in regard to its scope. The work of the session was organised in July, 1914, before the outbreak of war, on the traditional lines, and to a large extent it was carried out with a close adherence to the "Announcements" so published, partly because at the period of enrolment large numbers of our fellow-countrymen had failed to realise what the war meant, and therefore made arrangements to carry through the winter in the usual way. Scarcely more than an average number of classes had to be closed because of failure in enrolment, and it was only as the session progressed that the leakage became very serious.

The work will, as usual, be referred to in two main divisions, namely, (1) *Educational Work* and (2) *Social and Recreative Work*, which will be dealt with in the order named.

On the Educational side, when enrolments were started in September it was found that during the vacation, and following closely upon the outbreak of war, a number of students who would have re-entered the classes under normal conditions had either enlisted in the ranks or obtained commissions in His Majesty's Forces. Eventually, when the enrolments were made up at the end of the session, it was found that the total number of students during the session had been 1748, as against 2101 in the preceding session. The numbers, however, are not strictly comparable, for reasons which will be given presently.

The entry of new students in September in the day classes of the Engineering Day College was a record entry both in number and quality, and in consequence the total enrolments in this college for the session showed a very slight decrease, notwithstanding the fact that a large proportion of those students who were entitled to re-enter the college for higher courses failed to do so, as they had already joined the colours. Although, however, the enrolments were thus maintained, the second, third, and fourth-year classes, in which were the more senior students, gradually diminished as time went on by the members obtaining commissions in the army or taking up other urgent war work. The result was that by the end of the session one of the sections had ceased to exist and the others had been reduced to much smaller numbers than at the commencement. The first-year courses were, however, still in full vigour.

The evening courses, on the other hand, started with a considerable reduction in numbers, but on analysis a great part of this reduction was found to be due to causes quite unconnected with the war. Thus, the large Post Office workmen's classes of the preceding session had been found to be much too large for efficient handling, and in July, 1914, it had been decided to reduce them by two-thirds, involving a loss of nearly 200 students. The Junior Technical Institutes also took a heavier toll of the new applicants for entrance than in the preceding year, which was the first year of their existence. Eliminating these disturbing elements the net falling-off due to the war was estimated to be about 24 per cent, a much larger proportion than in the day courses, but so distributed that, as has already been remarked, most of the classes were formed and started.

The effect of the drain which at once commenced by the

enlistment of enrolled students is shown more conclusively by the student hours worked during the session, a test which has always been regarded in these reports as more real than the counting of the individuals enrolled or of the class entries. These student hours fell from 121,625 to 78,956, which is much more than 24 per cent. More eloquent still is that the number of hours worked by each individual student fell from 70.6 to 48, these figures being obtained by dividing the total number of student hours by the total number of individual students, no allowance being made for students who had only attended two or three times.

As usual the work continued to receive the cordial support of the trades affected. For the eleventh year in succession the Principal was able to place, without payment of any premiums, the whole of the second and third-year engineering students in commercial workshops for the summer. In fact this was easier than usual, because by Easter the loss of skilled workers was making itself felt in all engineering trades.

Further appreciation was shown by the Optical Society's Fund contributing again a substantial amount in support of the Technical Optics classes at the "Northampton." This was particularly gratifying at a time when it was being forced upon the attention of thinking men that the Governing Body had been patriotically justified in pressing on the authorities the necessity for establishing a national school of technical optics. One need only refer to the late

Lord Roberts' almost despairing appeal for field glasses, and the much more recent action of the Ministry of Munitions in commandeering the whole optical stock of the country in these and other optical appliances for the use of the Forces. Such a thing has never happened in this country before, and we should see to it at once that the initial steps are taken now to prevent it occurring again whatever unforeseen events may happen.

The prize list in the hands of those present gives the successes of the students in both external and internal examinations during the session. The number of students presented for the examinations in the Faculty of Engineering of the University of London this year was three in the Final and eleven in the Intermediate. The numbers so entered had been materially affected, however, especially as regards the Final examination, by the war. It is, therefore, gratifying to note that of the three students presented two passed with First Class Honours and the other one with Second Class Honours. In the Intermediate examination seven students passed, being the same number as in the preceding year.

In the City and Guilds of London Institute Examinations, the large decrease in the number of students attending the classes affected the number of candidates presented, and consequently certificates were awarded to 67 individual students only, as against 101 in the preceding session. In addition, four prizes and medals were awarded to students of the Polytechnic. In the competition for Scholarships and Exhibitions offered by the London Council, 13 students were successful, as against 23 in the preceding session, this falling-off being entirely due to war influences.

On the other hand, the number of certificates awarded on results of examinations by the St. John Ambulance Association showed, as might be expected, a large increase, being 96 as against 28 in the preceding session. Many of these students were enrolled in a Voluntary Aid Detachment, formed three years ago, and in which 110 members have been enrolled since its formation. The full number for such a detachment in normal times is twenty-five, but the restriction was removed early in the war. Many of the members are now on active service and many are waiting to serve; many, unable to take up active service, which requires the full time of the individual, are willingly giving their services to help in hospitals in the evening after working hours.

In the Institute prize lists—that is, the internal one—there are the usual substantial prizes offered by the Wor-

shipful Company of Skinners for all departments of the Institute's work. In addition there are the special prizes, which have now been offered for so many years by the Royal Society of Arts and by Mr. W. R. Corke, for students of the Clerkenwell Crafts School, and by Messrs. Aitchison and Co. for students of the Technical Optics Department. The cordial thanks of the Governing Body have been given to the donors of these prizes, which are specially valuable as showing the appreciation of the trades mentioned for the work of the Polytechnic.

Before speaking of the non-educational war work, which has absorbed a very large part of the activities of the staff and the students during the latter part of the session and through the long vacation, brief allusion may be made to the Roll of Distinction, copies of which, it is hoped, will be ready for distribution this afternoon. This roll shows that 22 members of the staff, 226 students, and 119 members of the Polytechnic, making 367 in all, have joined the colours. Of these it will be noted that over fifty have obtained commissions in one or other of the services. The Roll of Honour which appears at the beginning of the Roll of Distinction shows the names of those who have given their lives for the service of their country or who have been wounded in that service. It is with sincere and profound regret that one finds that there are seven in the first category and six in the second. Both these lists, moreover, are probably very incomplete, as it is difficult to get students and their relatives to send the necessary information to the Principal.

With regard to the Roll of Distinction, it may be noted that the Governing Body has decided that every student or member who has gone to the Colours may be readmitted to the Polytechnic on his return to civil life, taking up his work and his privileges, as far as possible, at the point at which they were interrupted on his enrolment with the colours.

On the Social Side the influence of the war has been very great. All departments of the work show decreases, although strenuous efforts have been made to keep up the numbers. The conspicuous former successes which have been reported annually of the various clubs in competitions have been interrupted by the disappearance of the competitions themselves and also of the competitors, the majority of whom have gone to the front. The Saturday evening entertainments were continued throughout the season, but although the audiences were substantial they were not as large as heretofore. The attempt to run these entertainments during the current season has had to be discontinued for want of the necessary public support.

What will probably be more interesting to those present than details of the diminishing work, whether educational or social, of the ordinary type, will be the War Work which has been undertaken by the Polytechnic during and since the period under review. Early in the session 1914-15 the Governing Body offered to place at the disposal of the Government for utilisation in furtherance of the war the whole of the equipment and staff of the Polytechnic. This offer was formally made immediately after Christmas, though there had been tentative informal offers earlier. For some months nothing came of the offers, but after Easter they were taken up, and may be summarised under three different headings.

First, as regards educational work, courses for drafts from the artillery divisions of the new armies were organised, and, commencing in the middle of May, have been continued practically without intermission down to the present time. The courses consisted of classes in field telephony, in range-finding, and in plane table work and map-reading. Altogether 897 individual students have passed through these courses, and very cordial thanks have been received from Whitehall and from the divisional headquarters, as well as from individual brigades, the letters expressing high appreciation of the value and importance of the work done.

Another line of work was the placing of the equipment

and staff of the Polytechnic at the disposal of the Government for experimental work. One of the senior members of the staff was lent to the War Office entirely for some months. A fair amount of experimental work was also done in the building, but as it was necessarily of a confidential nature it is, of course, quite impossible to give details. It may, however, be remarked that no charge was made to the Government for any of this work beyond the out-of-pocket expenses incurred in carrying on the work of the absent members of the staff.

The third, and probably the most interesting section of the work, consisted in the manufacture of munitions, the work undertaken being of the highest type. To clear the decks for this work the ordinary day session of the Engineering College was closed before the advertised time, and the students having been tuned up by a preliminary period of exercises in the workshops, organised on a factory basis, actual manufacture of the munitions was commenced on July 1. This has continued without intermission ever since, the workshops being manned from the start by the engineering day students for the rough work of manufacture and by the highly-skilled staff of the engineering departments, with some outside assistance, for the higher work.

In order that this work may be proceeded with at the highest possible rate of output, as well as for other reasons, the senior courses in the Engineering Day College are not being run this session, all available students being utilised as full-time munitions workers. Only Government orders have been accepted for the work, and the Government is only being charged actual out-of-pocket expenses, no charge being made for the services of the skilled members of the staff given in the time which the Institute can claim from them, and no charge for establishment expenditure except such as is directly due to the factory work itself.

In view of these three lines in which the Polytechnic has been doing important work for the country in connection with the war, the Principal ventures to assert that the "Northampton" may claim to have "done its bit," and to be still doing it, in the full and confident belief that it is bringing nearer the time when we shall all welcome the victorious termination of the war.

In conclusion the Principal desires to express his keen appreciation of the effective and loyal assistance given to him by every member of the staff in carrying out not only the usual work, both educational and social, of the Institute, but also the very special and strenuous work which has been referred to in the last part of this report.

PROCEEDINGS OF SOCIETIES.

FARADAY SOCIETY.

Ordinary Meeting, December 8, 1915.

THE meeting was devoted to a general discussion on "The Corrosion of Metals, Ferrous and Non-Ferrous," and it was presided over by Sir ROBERT HADFIELD, F.R.S., President, who introduced the subject under discussion with an address dealing principally with the corrosion of steel alloys.

In emphasising the importance of the subject the author pointed out that the annual losses of iron in the world by corrosion amounted to hundreds of thousands of tons. Four types of corrosion were met with: (a) from ordinary atmospheric effects, (b) from special atmospheric conditions, e.g. in manufacturing centres, (c) in special media, such as gases or acid liquids, (d) by heating effects. Studies of the alloys of iron by which corrosion can be governed or corrected and this deterioration resisted, were of great benefit to mankind. He (the speaker) and Dr. Friend were submitting specimens of the special alloys which he had produced during the last twenty years to an exhaustive examination of their corrosive qualities. Some

of the results were embodied in Dr. Friend's paper. He gave some particulars of other work on the corrosion of steel alloys which had not yet been published. Exaggerated claims had been made for the resistive action of nickel steels. It might be very resistant with high nickel content, but once corrosion commenced even these corroded badly, and commercial nickel steels did so to an even greater extent.

A special chromium steel, called "stainless" steel, containing some 10 to 12 per cent chromium and about 0.3 to 0.4 per cent carbon, has recently been largely used for table cutlery, as it was found not to tarnish in contact with food or acids. This confirmed results obtained by the author in 1892 as to practical freedom from ordinary rust conferred on iron by about this percentage of chromium. The mechanical properties of these steels after suitable heat treatment were excellent, and figures were given. Strangely enough the "stainless" steel did not give a very good test in 10 per cent sulphuric acid, and it would be necessary to make full and proper tests to determine whether high chromium steels were suitable for structural work, such as dock gates, where corrosion had to be resisted.

The paper concluded with an abstract of the exhaustive acid tests made by Dr. A. S. Cushman and the author on various series of alloy steels.

Dr. C. H. DESCH (Glasgow) sent in a paper on "Physical and Mechanical Factors in Corrosion."

All methods of studying corrosion which involve the determination of the loss of weight of the corroded metal, without distinguishing the different forms in which the constituents are removed, confound together a number of distinct phenomena. Corrosion is usually due to the formation of local couples, due to chemical or physical heterogeneity in the metal or alloy. Examples of both cases are given. Besides the physical condition of the metal, that of the oxide layer or other product of corrosion has to be taken into account. Some such layers are tough and coherent, others are porous and friable. The protective action of certain additions, such as that of tin or brass, is explained by the formation of protective layers of basic salts. Photo-micrographs are given, showing the way in which corrosion takes place in yellow brass, Muntz metal, and light aluminium alloys. The method of carrying out comparative tests of metals in order to determine their probable resistance to corrosion is also described, and some of the results are recorded.

Dr. J. NEWTON FRIEND (Worcester) read a paper on "The Relative Corrodibilities of Iron and Steel."

In view of the present economical crisis it becomes increasingly important to conserve our stores of iron and coal and to reduce to a minimum all waste of metal by corrosion. The question is often asked, Which is the more corrodible, iron or steel? In order to answer this question satisfactorily it is necessary to specify the nature of the corroding media which the metal is expected to resist, and also the standard of corrodibility to be adopted. Thus, for example, certain types of iron and steel are particularly resistant to atmospheric corrosion, whilst others are less affected by acids. Again, some kinds of iron are readily pitted and are thus unsuitable for piping, whilst others tend to corrode fairly uniformly all over. The question, therefore, is not quite as simple as it looks, but resolves itself into a wider problem, not so much as to whether iron is better than steel or *vice versa*, but rather which is the best type of iron or of steel for any particular purpose: It is probable that certain makes of wrought iron will prove most useful in certain circumstances, whilst under other conditions the palm will have to be given to steel.

Mr. LESLIE AITCHISON (Sheffield) read a paper entitled "The Influence of Composition upon the Corrosion of Steels."

In Part I. of this work the results of experiments were presented showing the action of 3 per cent sodium chloride and 1 per cent and 10 per cent sulphuric acid

upon a series of steels containing (1) carbon, (2) a fixed proportion of carbon and a varying proportion of either tungsten, vanadium, chromium, cobalt, (3) a varying proportion of carbon and a fixed proportion of the above elements and also nickel and manganese, and (4) some copper steels. The present two parts show (a) the action of tap-water upon these same alloys, and (b) the microscopic features of interest in the whole series.

Parts I. and II. show that in general the addition of a small proportion of any third element increases the corrodibility of a steel. Carbon alone does not increase the corrodibility at small percentages, but beyond 0.5 per cent the increase is distinct. The third element increases the action in most cases up to about 5 per cent, and beyond that takes a course decided by the element in question and by the attacking medium. In only one case (that of chromium) is there any permanent decrease of corrodibility, and this is found in the case of each medium except 10 per cent sulphuric acid, in which there is a violent increase. In all the alloys under review these high chromium steels are almost the only ones to show any real advantage over pure mild steel.

The microscopic examination shows various features of interest. Ferrite is always attacked, and presumably by the usual process of the production first of etching pits which spread gradually over the area under attack. The action is helped by various causes. Pearlite if present is attacked apparently in the ferrite only, the removal of the carbide of the pearlite being mechanical rather than chemical—that is, the matrix of ferrite in which the carbide is embedded is removed by the corrosion, and then the carbide drops out. Solid solutions act like ferrite if they are attacked at all. Carbides are always unattacked, and appear to act as aids to the corrosion by providing a definite cathode for the anode of the ferrite or solid solution. The action of twinning and of the intercrystalline matrix in the metals in increasing the corrosion is also demonstrated. It is proved very conclusively that non-homogeneity is not necessarily an aid to corrosion, one of the least homogeneous of the materials examined being corroded least.

Mr. S. WHYTE (Redhill) read a "Note on the Corrosion of Iron and Steel."

The contribution deals with the relation between "overheating" in a mild steel and the subsequent behaviour towards corrosion.

A water pipe which was found to have corroded rather quickly in a soil of yellow clay showed a badly overheated structure. Another pipe of the same chemical composition, which was laid down at the same time, had not corroded so badly, and showed a correspondingly better micrographic structure.

An accelerated test was used to investigate the nature of the process of the corrosion in this case, and specimens of an overheated steel and a normalised one were prepared from bars of steel of 0.28 per cent C. and 0.55 per cent respectively. An applied e.m.f. was used, and the specimens were made the anode, the electrolyte being a dilute solution of sodium chloride. The iron which dissolved out was estimated as the corrosion product, and the average of the results shows that under these conditions the corrosion product of the overheated specimen was about 20 per cent more than that of the normalised one.

While the results of the accelerated test-point to a decided increase in the amount of corrosion due to overheating, it is admitted that the method is only suitable for studying the initial stages and the subsequent chemical actions might exert an opposite influence. The grain of the overheated steels being coarse and open, the chemical products of corrosion are not likely to be so adherent as with fine-grained ones, so that it is probable the subsequent chemical actions are more or less on a parallel with the initial ones.

DISCUSSION.

Dr. E. K. RIDEAL in a written communication said that a precise definition was necessary before the mechanism

of corrosion could be properly discussed, and he suggested the following:—"Corrosion results from an irreversible chemical change proceeding with a small velocity and taking place on the common surfaces between two or more phases, the products of which change are continually removed from the sphere of action." He went on to emphasise the significance of the action being a surface one, and pointed out that corrosion generally takes place on the surface of a conductor—a corner-stone of the electrolytic theory. Cohen's work on allotropy tends to show that even pure metals may corrode, as allotropic forms with different physico-chemical properties can exist. Illustrations are given of variations in corrosion in the different physical states of copper. It is shown how the electrolytic theory explains why very small traces of certain impurities can greatly accelerate corrosion, and possibly also the laminated character of some rust formations. An important factor in corrosion is the removal, usually by oxidation, of the hydrogen liberated in the cathodes of the small surface couples. This explains the observation that the rate of corrosion of iron and steel pipes increases with the rate of flow of water through them up to a maximum.

Dr. WALTER ROSENHAIN, referring to the specimens of uncorroded ancient iron and steel exhibited, thought these would probably corrode in modern air, especially in Europe. There might be protective layers of cinder in the ancient iron. The resistance to corrosion of "stainless" and similar steels might in the same way be due to surface conditions; perhaps the surface amorphous layers contained a protective element. A rustless steel he had examined rusted when roughened, although when polished it remained bright for months.

The decrease of corrosion of steel with the increase of carbon up to 0.35 or 0.4 per cent. observed by Mr. Aitchison was noteworthy; it was the second property of steel reaching a critical point at that concentration. He attached some weight to the action of inter-crystalline cement as a possible factor in corrosion, although difficulties arose, for there should be a connection between grain size and corrosion, which was not the case according to Mr. Aitchison. All laboratory experiments on corrosion had to face the criticism that they only considered the beginning of corrosion, whereas what mattered was rate of corrosion throughout the mass. This consideration was also an objection to the electrolytic theory.

Mr. L. PENDRED, referring to Dr. Rosenhain's last remarks, said Mr. Harbord and he had recently carried out a series of tests on industrial lines. Large pieces of various steels and irons as they were received from the makers were exposed to varying practical conditions. The results unfortunately were quite inconclusive. On the average all steels were about equally resistive, and iron was no better and no worse. Some curious facts were noticed. Thames water had little corrosive effect, but London air even surpassed sea-water.

Dr. T. M. LOWRY referred to a test of nails in water in a beaker with filter paper on the top. All the rust was on the top of the beaker above the filter paper and was not on the nails at all.

Mr. A. F. DISMORE suggested that corrosion should be dealt with not as taking place from the outside to the inside, but from the inside to the outside. It was possible to convert cast-iron with a high carbon content into non-corrodible steel by an electrolytic process which he had hit upon.

Mr. ARNOLD PHILIP remarked that London tap water, hard and chalky, was more corrosive than would be the soft Sheffield water used in Mr. Aitchison's experiments. The units used in measuring corrosion should be standardised.

Mr. L. AITCHISON, replying to Dr. Rosenhain, said there was a difference between the inter-crystalline material in pure metals and in the alloys he had tested.

Dr. J. N. FRIEND thought his own standard method of measuring corrosion, taking a constant of 100, was the

simplest, and it could be applied to pitting where Mr. Aitchison's could not.

Mr. ARNOLD PHILIP read a paper on "*The Zinc-Copper Couple Hypothesis of Brass Corrosion.*"

In lieu of the theory that the corrosion of two-phase brass by sea-water is due to the action of electrolytic currents set up by minute couples of adjacent crystals of metals of difference phase, the author supports the view that it is minute zinc-copper couples that act as electrical cells, and the paper contains evidence in favour of this theory. Both α and β brass consist of solutions of zinc in copper, and the surface of such brass may reasonably be considered to consist of surfaces of zinc and copper in close contact. The subject is considered under the headings of (1) auto-corrosion, (2) contact corrosion, (3) external current corrosion.

Auto-corrosion.—The current flows from the zinc element, where in the case of immersion in sea-water zinc chloride is formed, to the copper element, where caustic soda is formed and hydrogen deposited on the copper. If no oxygen is present polarisation will stop further action and corrosion will cease; if oxygen is present dezincification and separation or corrosion of copper will occur. It further follows from the author's theory that raising the temperature, increasing the strength of the electrolyte or its oxygen content or agitating it, all increase corrosion, and this is all borne out by experiment. The theory is also shown to support the observation that higher zinc content, such as exists in Muntz metal, lowers the rate of corrosion, a fact difficult otherwise to explain, for a 70/30 brass is a single-phase, while a 60/40 brass is a two-phase system.

Marked and sharply localised dezincification areas in brass often occur beneath white crystalline deposits of what is apparently zinc chloride, and the effect is shown to be explicable on the zinc-copper couple hypothesis, although more investigation on this phenomenon is desirable. The increased corrosion of brass in sea-water on a rough surface is also shown to be explicable on the author's hypothesis. Experiments on the behaviour of brass in solutions of zinc and copper salts to clear up some outstanding difficulties are in progress.

Contact-corrosion is due to the action of sea-water upon brass in contact with another solid conductor which may be either more electro-negative than copper, such as coke, or more electro-positive than zinc, such as magnesium, or intermediate between the two, such as copper, or cuprous oxide, or zinc. On the basis of the author's theory expressions are deduced giving the relative magnitude of the corrosion in these different cases, and these are shown to agree with observation.

The External Current Corrosion of Brass.—This occurs where current passes from brass into an electrolyte, and the theory shows that unlike in auto-corrosion the γ -phase in such an alloy as Muntz metal is more slowly attacked than the β -phase, which is the richer in zinc. This is borne out by the experiments of Desch and Whyte, which are discussed from the point of view of the author's theory.

Mr. W. E. GIBBS, M.Sc. (Liverpool), in his paper dealt with the "*Sea-water Corrosion of 70/30 Brass.*"

After distinguishing between "complete" corrosion, "selective" corrosion, and "localised" corrosion, he described the influence of a number of important factors upon the rate and character of the corrosive attack, and compared the behaviour of 70/30 brass with that of pure Cu and pure Zn. The rate of corrosion of copper-zinc alloys diminishes as the zinc content increases, and reaches a minimum at the composition which corresponds to equal atomic concentrations of zinc and copper. A further increase in the concentration of zinc leads to a gradual increase of the rate of corrosion until pure zinc is reached.

Up to 50° C. the initial rate of corrosion of 70/30 brass is greater at high temperatures than at low. At the same

time the rapidity with which the initial rate of corrosion falls off with time is greater the higher the temperature. At 60° C., however, the initial rate of corrosion is smaller than at 15° C.

Aerated sea-water is more corrosive than stagnant sea-water. The effect of aeration is smaller the higher the temperature, until at 50° C. it is almost nothing. At 60° C. aeration diminishes the rate of corrosion.

Diluted sea-water attacks 70/30 brass more slowly than ordinary sea-water. At the same time the proportion of Zn in the corrosion product is greater the more dilute the sea-water. It is also found that the corrosion of zinc is very greatly facilitated by the presence of CO₂ in solution. Oxy-salts of copper or zinc when in contact with brass appear to promote selective corrosion. Zinc oxychloride is formed at high temperatures (80°-100° C.) and facilitates the selective corrosion of zinc. An oxychloride is formed at lower temperatures (15° C.-50° C.) and facilitates the selective corrosion of copper.

Hard-drawn 70/50 brass dissolves less rapidly than the annealed alloy, but undergoes dezincification more readily.

Electrical contact with carbon accelerates the corrosion of 70/30 brass in sea-water and promotes dezincification. Localised action is probably caused in many cases by a lack of homogeneity in the alloy itself. This may be due, amongst other things, to mechanical strain, dissolved Cu₂O, and differences of temperature along the tube. Mr. Gibbs thinks that a solid solution of zinc and copper is intermediate in character between a physical mixture and a chemical compound. Possibly there exists a kind of "physical" combination in which the chemical character of the constituents is not changed but only modified.

DISCUSSION.

Mr. ULICK R. EVANS could not agree with the theory of Mr. Arnold Philip. If brass were a mosaic of zinc and copper, corrosion would take place far more rapidly than is the case. Moreover, it should corrode in sea-water even if free from dissolved oxygen, for if the zinc is kept free from basic salt it would go on dissolving in spite of the deposition of hydrogen on the copper. Further, on Mr. Philip's hypothesis a Daniell cell in which the zinc has been covered (by immersion) with black copper should behave similarly to one in which a similar use of brass has replaced the zinc. This is not the case. If brass were simply a mosaic of zinc and copper, the p.d. should be that of the more electropositive metal; it behaves, however, as a solid solution. The equilibrium diagram does not support the view that there is no chemical combination between the constituents of brass. The presence of a corrosion-residue of pure copper can be explained by a process of solution and redeposition on the less electropositive portion of the metal. Microscopic examination would throw light on the point.

Prof. H. C. H. CARPENTER thought too that Mr. Philip's theory was quite untenable. The evidence was quite opposed to the view that both the α and β phases of brass consisted of solutions of zinc in copper. The equilibrium curve showed that six phases separated from the liquid, and in such a complex system it was highly improbable that minute particles of zinc and copper could exist side by side. The hypothesis given by Mr. L. Gibbs that a solid solution of zinc and copper was intermediate between a physical mixture and a chemical compound seemed more probable.

Prof. A. K. HUNTINGTON supported Dr. Carpenter's view.

Dr. W. ROSENHAIN was disposed to agree both with Prof. Carpenter and Mr. Philip. The question turned on the conception of an intermetallic compound. Bragg's work altered the old view that it was a crystal built up of molecules. Could an atomic couple exist or could it produce a current? It seemed unlikely on the face of it.

Mr. W. E. GIBBS said the facts did not agree with Mr. Philip's hypothesis. Zinc in contact with copper

should go into solution more easily than zinc alone, and the copper should not dissolve at all. But zinc in brass dissolved less rapidly than pure zinc, and copper dissolved normally as fast as the zinc. The e.m.f. of brass in seawater resembled that of copper rather than zinc, whereas a mixture of zinc and copper had the same e.m.f. as pure zinc.

Mr. ARNOLD PHILIP, in reply, said he had put forward his hypothesis not as proved but to be considered. At the same time he did not see how corrosion could be explained unless something in the nature of couples acting electrolytically were present.

At the conclusion of the Discussion, Mr. Elliott Cumberland gave a Demonstration of his Electrolytic Process for Preventing Corrosion of all Metals Immersed in Liquids.

The method consists of introducing a higher counter electromotive force than that causing the corrosive action, and has achieved success in practical working conditions, and proved itself to be the only effective method of overcoming the dezincification of condenser tubes. Continuous current is supplied by a dynamo, working at 20 volts, to pieces of iron suspended in the liquid and suitably insulated from the vessel being protected. All agents to corrosion are transferred from the structure to the inserted iron, which is connected as anode, and any detrimental differences of potential are overcome.

The structure is protected at the expense of these iron anodes, which are designed to last from eighteen months to two years. The cost of current is very small, owing to the low voltage used.

For many years this system has been used in all types of steamships, and many large power plants on shore, and has proved successful in severe cases where other methods had failed.

The regular working of this electrolytic system also has a remarkable effect in removing hard scale from heating surfaces, &c., and preventing its further formation.

The system may be applied to all types of steam boilers, economisers, feed-water heaters, tanks, propellers, and stern frames of ships; in fact all metals immersed in, or in contact with, water or other corrosive metals.

The amount of zinc necessary for the protection of the internal surfaces of steam boilers is stated to be as one square foot of zinc to 50 square feet of heating surface. In the boilers of the *Lusitania* and *Mauretania* there are 84 zinc plates in each boiler, and these are renewed four times per year. Each plate is of pure rolled zinc, and weighs about 20 lbs. At the present price of zinc this would mean a cost of about £1 per plate, or an annual cost per ship of £8400.

Numerous examples of non-corrodible metals and alloys and of interesting specimens of corroded metals were exhibited at the meeting by the President and by Dr. J. Newton Friend, and Mr. Robert Lennox had an exhibit of a variety of articles made of his well-known non-corrodible ferro-alloy known as "Tantiron." Among the exhibits were an Egyptian hatchet and other implements of iron lent to the President by Prof. Flinders Petrie. The hatchet, although at least 2500 years old, was apparently in the same state as when it left the forge.

A Table of Food-stuffs.—The East Anglian Institute of Agriculture at Chelmsford has prepared a table, dealing with food-stuffs, which can be had gratis by farmers resident in Essex and Hertfordshire, on application to the Principal. The table, which will be of great value to farmers, in view of the present high prices of all feeding stuffs, gives (i.) the composition and food units of a great number of food-stuffs, including several new foods which have come into prominence owing to the war; (ii.) a method of valuation of food-stuffs, with examples, which should give the farmer much assistance in selecting the cheapest suitable foods.

NOTICES OF BOOKS.

The Molecular Volumes of Liquid Chemical Compounds. By GERVAISE LE BAS, B.Sc. (Lond.). London, New York, Bombay, Calcutta, and Madras: Longmans, Green, & Co., 1915.

IN this monograph the theory of molecular volumes from the point of view of Kopp is applied to the study of the constitution of organic compounds and of compounds of nitrogen, phosphorus, and sulphur. The author has brought together and carefully sifted the experimental data which are to be found in Clarke's "Constants of Nature" Part I., the "Chemiker-Kalender," and many papers in English and German scientific journals. He shows that the additive principle is prominent, but not unqualified. He discusses the question of the variation in the volumes of the atoms and is forced to take into consideration a larger number of atomic value than has been adopted heretofore. The strong influence of constitution is also discussed at some length, especially that of ring structure. It is pointed out that many questions require much fuller study before definite pronouncements can be made upon them, as, for example, the special influence of groups, and the monograph will be indispensable to those who, before beginning research work on the subject, wish to know exactly what has been done by other workers.

The Scientist's Reference Book and Diary for 1916. Manchester: Jamess Woolley, Sons, and Co., Ltd.

THIS is a handy little book, about 6 by 4 inches, leather bound, published at 2s. In addition to the calendar, it contains a well selected set of tables and constants in common use by scientific men and students, extending to more than 100 pages, as well as an ample allowance of blanks for memoranda and the usual insurance policy.

CORRESPONDENCE.

ANNEALING OF GLASSWARE.

To the Editor of the Chemical News.

SIR,—Practically all glassware is subjected to an annealing operation to remove strains induced during manufacture, but it is not generally recognised that every glass has a particular temperature to which special consideration should be given in order to obtain perfect annealing.

We have devoted much attention to the determination of these critical temperatures, and as we have no doubt many English manufacturers would esteem such information for their own products we shall be pleased to receive their inquiries for undertaking this work.—We are, &c.,

ADAM HILGER, LTD.

75A, Camden Road, London, N.W.

MEETINGS FOR THE WEEK.

MONDAY, Jan. 3rd.—Society of Chemical Industry, 8. Exhibit of Chemicals and Apparatus. Papers will also be read.

TUESDAY, Jan. 4th. } Royal Institution, 3. (Christmas Lectures,
THURSDAY " 6th. } adapted to a juvenile auditory). " Wireless
SATURDAY " 8th. } Messages from the Stars," by Prof. H. H. Turner.

TUESDAY, 4th.—Röntgen Society, 8.15. (At the Institution of Electrical Engineers, Victoria Embankment, W.C.). "Some Observations upon the Occurrence of Uranium," by J. H. Gardiner. Model of a New Therapeutic Tube Stand, by P. J. Neate. Lantern Slides Illustrating Bullet Injuries, by C. A. Schunk. New Form of Screen Rest, by N. S. Finzi. A New Localiser, by Dr. Harvey. Exhibition of a Dubilier X-ray Apparatus.

WEDNESDAY, 5th.—Royal Society of Arts, 3. (Juvenile Lecture). "Crystallisation," by Prof. J. M. Thomson.

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